Electronic Supplementary Material (ESI) for Dalton Transactions.

Tuning the Cytotoxicity of Ruthenium(II) *para*-Cymene Complexes by Mono-Substitution at a Triphenylphosphine/ Phenoxydiphenylphosphine Ligand

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Supporting Information

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Table 1S. Comparison of selected IR and NMR data for ruthenium complexes and related compounds.

Compound	**IR [a]: ũ/cm^{-1}**			**NMR [b]: δ/ppm**		
	ν(C=O) [1]	**ν(O-Ar) [2]**	**ν(P-O) [2]**	**^{13}C δ(CO$_2$)**	**^{31}P (Δ$_{complex}$δ)[c]**	**^{29}Si**
Ph$_2$P(4-C$_6$H$_4$OSiMe$_2{}^t$Bu)	-	1174m	-	-	-6.8	21.2
1	-	1176s	-	-	23.2 (+30.0)	21.7
Ph$_2$P(4-C$_6$H$_4$Br)	-	-	-	-	-6.5	-
2	-	-	-	-	24.4 (+30.9)	-
[RuCl$_2$(η^6-*p*-cymene){κ*P*-Ph$_2$P(4-C$_6$H$_4$OH)}] [3]	-	1178s	-	-	22.9	-
Cl$_2$CHCO$_2$H	1731s	-	-	170.3	-	-
3	1785m-sh, 1768m	1168s	-	162.5	24.0	-
Ph$_2$P(OPh)	-	1218s	868s	-	110.7	-
4	-	1208s	889s	-	113.7 (+3.0)	-
Ph$_2$P(O(2-C$_6$H$_4$SiMe$_2{}^t$Bu))	-	1200s	870s	-	108.3	3.3
5	-	1185s	885s	-	120.3 (+12.0)	3.0
6	1697s, 1674s, 1666s-sh	1180s	892s	165.4	124.3 (+16.0)	3.4
PPh$_3$ [4]	-	-	-	-	-4.7	-
[RuCl$_2$(η^6-*p*-cymene)(κ*P*-PPh$_3$)]	-	-	-	-	24.2 (+28.9)	-
[Ru(C$_2$O$_4$)(η^6-*p*-cymene)(κ*P*-PPh$_3$)]	1688s, 1666s, 1652s	-	-	167.1	29.8 (+34.5)	-
[(Ru(C$_2$O$_4$)(η^6-*p*-cymene)(H$_2$O)]	1687w-sh, 1665s	-	-	166.9	-	-

[a] Solid-state or liquid film (Cl$_2$CHCO$_2$H). [b] CDCl$_3$ solution except [RuCl$_2$(η^6-*p*-cymene){κ*P*-Ph$_2$P(4-C$_6$H$_4$OH)}] (DMSO-d$_6$) and [Ru(C$_2$O$_4$)(η^6-*p*-cymene)(H$_2$O)] (D$_2$O). [c] Chemical shift difference upon complexation: Δ$_{complex}$δ = δ(M-PR$_3$) - δ(PR$_3$).

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1 J. Fujita, A. E. Martell and K. Nakamoto, *J. Chem. Phys.*, 1962, **36**, 324-331.

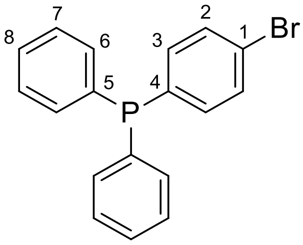
2 J. Chatt and B. T. Heaton, *Spectrochim. Acta A*, 1967, **23**, 2220-2221.

3 L. Biancalana, L. K. Batchelor, A. De Palo, S. Zacchini, G. Pampaloni, P. J. Dyson and F. Marchetti, *Dalton Trans.*, 2017, **46**, 12001-12004.

4 J. Schraml, M. Capka and V. Blechta, *Magn. Reson. Chem.*, 1992, **30**, 544-547.

Synthesis and spectroscopic characterization of $Ph_2P(4\text{-}C_6H_4Br)$.[5]

Chart 1S. Structure of $Ph_2P(4\text{-}C_6H_4Br)$ (numbering refers to carbon atoms).



In a 50 mL Schlenk tube, n-BuLi (2.6 mL of a 2.5 M solution in hexanes, 6.5 mmol) was slowly added (15') to a solution of 1,4-dibromobenzene (1.250 g, 5.30 mmol) in Et_2O (15 mL), at -50 °C under vigorous stirring. The reaction mixture was stirred for 1 hour and allowed to warm up to -5 °C affording a pale yellow solution. Therefore Ph_2PCl (1.1 mL, 6.0 mmol) was slowly added (10') at -50 °C and the resulting yellow solution was allowed to reach ambient temperature. The slow formation of a colourless precipitate (LiCl) was observed. The suspension was stirred for 14 hours then filtered on a short silica pad (h 3 cm, d 4 cm), thus the product was eluted with Et_2O. A yellow oily residue was obtained after volatiles removal under vacuum. Addition of MeOH (5 mL) under vigorous stirring resulted in the formation of a colourless solid. The liquid was removed and the solid was washed with few mL of MeOH and dried under vacuum (40 °C). Yield: 1.01 g, 56%. Anal. Calcd. for $C_{18}H_{14}BrP$: C, 63.37; H, 4.14. Found: C, 63.25; H, 4.20. IR (solid state): $\tilde{\upsilon}/cm^{-1}$ = 3065w, 3045w, 3025w, 3013w, 3000w, 1970-1660w, 1639w, 1581w, 1571w, 1475m, 1433m, 1380m, 1351w, 1326w, 1307w, 1296w, 1259w, 1205w, 1180w, 1156w, 1118w, 1088m, 1068m, 1026w, 1009m, 998w-sh, 913w, 849w, 818s, 744s, 722s, 694s. ^1H NMR ($CDCl_3$): δ/ppm = 7.47 (d, $^3J_{HH}$ = 7.7 Hz, 2H, C2-H), 7.39–7.33 (m, 6H, C7-H + C8-H), 7.33–7.28 (m, 4H, C6-H), 7.17 (t, $^3J_{HH} = {}^3J_{HP}$ = 7.6 Hz, 2H, C3-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ/ppm = 136.7 (d, $^1J_{CP}$ = 11 Hz, C5), 136.6 (d, $^1J_{CP}$ = 12 Hz, C4), 135.4 (d, $^2J_{CP}$ = 20 Hz, C3), 133.8 (d, $^2J_{CP}$ = 20 Hz, C6), 131.8 (d, $^3J_{CP}$ = 7 Hz, C2), 129.1 (C8), 128.8 (d, $^3J_{CP}$ = 7 Hz, C7), 123.5 (C1). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ/ppm = -6.5.

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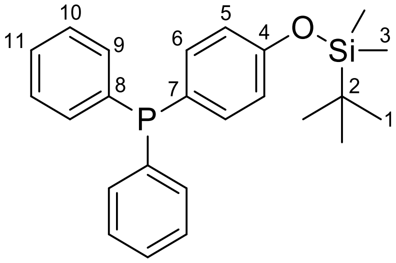
[5] R.A. Baldwin and M. T. Cheng, *J. Org. Chem.*, 1967, **32**, 1572-1577.

Spectroscopic characterization of ligands/intermediates.

1) $Ph_2P(4\text{-}C_6H_4OSiMe_2{}^t\!Bu)$.[3]

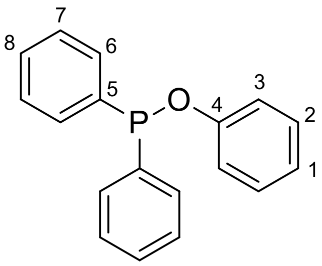
Chart 2S. Structure of $Ph_2P(4\text{-}C_6H_4OSiMe_2{}^tBu)$ (numbering refers to carbon atoms).



Colourless solid. Anal. Calcd. for $C_{24}H_{29}OPSi$: C, 73.43; H, 7.45. Found: C, 73.64; H, 7.41. IR (solid state): $\tilde{\upsilon}$/cm^{-1} = 3067w, 3054w, 2954w, 2927w, 2893w, 2855w, 1592m, 1496m, 1462m, 1471m, 1432m, 1403w, 1389w, 1360w, 1324w, 1277s, 1258s, 1174m ($\nu_{O\text{-}Ar}$), 1098m, 1068w, 1025w, 1007w, 912s, 830s, 804s, 779s, 744s, 695s, 672m. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.38 (s, 10H, PPh_2), 7.32 (t, $^3J_{HH}$ = $^3J_{HP}$ = 7.0 Hz, 2H, C6-H), 6.93 (d, $^3J_{HH}$ = 8.1 Hz, 2H, C5-H), 1.08 (s, 9H, C1-H), 0.30 (s, 6H, C3-H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ/ppm = 156.7 (C4), 138.0 (d, $^1J_{CP}$ = 11 Hz, C8), 135.6 (d, $^2J_{CP}$ = 21 Hz, C6), 133.6 (d, $^2J_{CP}$ = 19 Hz, C9), 128.6 (C11), 128.5 (d, $^3J_{CP}$ = 6 Hz, C10), 120.4 (d, $^3J_{CP}$ = 7 Hz, C5), 25.8 (C1), 18.3 (C2), 1.2 (C3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ/ppm = -6.8. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ/ppm = 21.2.

2) $Ph_2P(OPh)$.

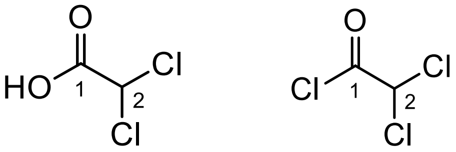
Chart 3S. Structure of $Ph_2P(OPh)$ (numbering refers to carbon atoms).



Colourless paste. IR (solid state): ṽ/cm^{-1} = 3070w, 3054w, 3036w, 3003w, 1970-1770w, 1593m, 1584m, 1573m-sh, 1490s, 1478s, 1456w, 1433m, 1392w, 1328w, 1307w, 1285w, 1218s ($\nu_{P\text{-}O\text{-}Ar}$), 1179m, 1166m, 1092m, 1070m, 1024m, 998m, 920w, 913w, 868s ($\nu_{P\text{-}O\text{-}Ar}$), 829m-sh, 758s, 746s-sh, 739s, 721s, 687s. ^{1}H NMR (CDCl$_3$): δ/ppm = 7.58 (td, $^3J_{HH}$ = $^3J_{HP}$ = 7.6 Hz, $^4J_{HH}$ = 1.9 Hz, 4H, C6-H), 7.41–7.34 (m, 6H, C7-H + C8-H), 7.28–7.22 (m, 2H, C2-H), 7.14–7.10 (m, 2H, C3-H), 7.00 (t, $^3J_{HH}$ = 7.3 Hz, 1H, C1-H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ/ppm = 157.5 (d, $^2J_{CP}$ = 10 Hz, C4), 141.0 (d, $^1J_{CP}$ = 17 Hz, C5), 130.7 (d, $^2J_{CP}$ = 23 Hz, C6), 129.9 (C2/C8), 129.7 (C2/C8), 128.6 (d, $^3J_{CP}$ = 7 Hz, C7), 122.7 (C1), 119.0 (d, $^3J_{CP}$ = 11 Hz, C3). ^{31}P{^{1}H} NMR (CDCl$_3$): δ/ppm = 110.7.

3) Cl_2CHCO_2H and $Cl_2CHCOCl$.

Chart 4S. Structures of Cl_2CHCO_2H (left) and $Cl_2CHCOCl$ (right) (numbering refers to carbon atoms).



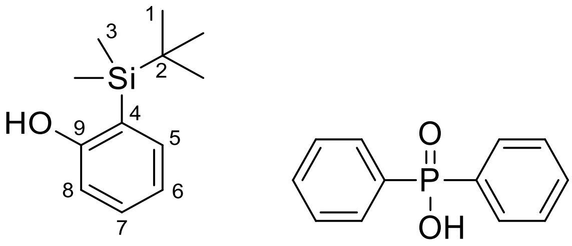
Cl_2CHCO_2H. Colourless liquid. IR (liquid film): ṽ/cm^{-1} = 3300-2800w-br, 3120w, 3018m, 2912w, 2689w, 2578w, 1731s ($\nu_{C=O}$), 1416 m, 1276 m, 1239m, 1191m, 919w, 816s, 775 m, 675m. IR (CH$_2$Cl$_2$): ṽ/cm^{-1} = 3460m-br, 1778s-sh, 1744s ($\nu_{C=O}$). ^{1}H NMR (CDCl$_3$): δ/ppm = 11.3 (s, 1H, OH), 6.01 (s, 1H, C2-H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ/ppm = 170.3 (C1), 63.8 (C2).

$Cl_2CHCOCl$. This compound was prepared by two different methods. A) In a 50 mL Schlenk tube, (COCl)$_2$ (0.10 mL, 1.2 mmol) and one drop of DMF were added to a solution of Cl_2CHCO_2H (20 µL, 0.24 mmol) in CDCl$_3$ (3 mL). The resulting colourless solution was stirred at ambient temperature for 3.5 hours. ^{1}H NMR spectrum of this solution indicated the complete conversion to the acyl chloride [^{1}H NMR (CDCl$_3$): δ/ppm = 6.12 (s, 1H, C2-H)]. B) A solution of Cl_2CHCO_2H (0.15 mL, 1.8 mmol) in CH$_2$Cl$_2$ (7 mL) was treated with PCl$_5$ (362 mg, 1.74 mmol). The resulting

colourless solution was stirred at ambient temperature overnight. IR spectrum of this solution indicated the complete conversion to the acyl chloride [IR (CH_2Cl_2): $\tilde{\upsilon}$/cm^{-1} = 1804s ($\nu_{C=O}$), 1778s].

Reactivity of $Ph_2P(O(2\text{-}C_6H_4SiMe_2{}^tBu))$ with HCl: synthesis of $2\text{-}C_6H_4(OH)(SiMe_2{}^tBu)$ and Ph_2PO_2H (diphenylphosphinic acid).

Chart 5S. Structures of $2\text{-}C_6H_4(OH)(SiMe_2{}^tBu)$ (left) and Ph_2PO_2H (right) (numbering refers to carbon atoms).



In a 100-mL round-bottom Schlenk flask, $Ph_2P(O(2\text{-}C_6H_4SiMe_2{}^tBu))$ (3.12 g, 7.96 mmol) was dissolved in a Et_2O/THF mixture (1:1 *v*/*v*, 30 mL) and treated with 37% HCl (1.35 mL, ca. 16 mmol) at 0 °C. The resulting pale yellow solution was allowed to heat to ambient temperature and stirred overnight. Therefore, O_2-free H_2O (15 mL) was added, and the massive precipitation of a colourless solid occurred. The suspension was filtered and the solid (Ph_2PO_2H) was washed with Et_2O and dried under vacuum. Volatiles were removed under vacuum from the filtrate mixture. The pale yellow oily residue was loaded on top of a silica column (h 4.5 cm, d 3.5 cm); impurities were eluted with petroleum ether and the title compound was eluted with CH_2Cl_2. Volatiles were removed under vacuum (50 °C) and a colourless solid ($2\text{-}C_6H_4(OH)(SiMe_2{}^tBu)$) was obtained.

Ph_2PO_2H.[6] Colourless needle-shaped crystalline material. Insoluble in chlorinated solvents, soluble in DMSO. IR (solid state): $\tilde{\upsilon}$/cm^{-1} = 3078w, 3057w, 2800-2500w-br, 2400-1800w-br, 1646m-br, 1588m, 1484m, 1438s, 1398w, 1338w, 1315w, 1224w, 1177m, 1152m, 1121s, 1069m, 1027m, 976s-

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[6] Integrated Spectral Database System of Organic Compounds, National Institute of Advanced Industrial Science and Technology, http://sdbs.db.aist.go.jp

sh, 957s, 931s-sh, 862m-sh, 754m, 726s, 691s. ^{1}H NMR (DMSO-d$_6$): δ/ppm = 7.82–7.59 (m, 4H), 7.57–7.35 (m, 6H). ^{31}P{^{1}H} NMR (DMSO-d$_6$): δ/ppm = 25.8.

2-C$_6$H$_4$(OH)(SiMe$_2$^{t}Bu).[7] Colourless crystalline solid. Yield: 1.32 g, 80%. Anal. Calcd. for C$_{12}$H$_{20}$OSi: C, 69.17; H, 9.67. Found: C, 69.38; H, 9.72. IR (solid state): $\tilde{\nu}$/cm^{-1} = 3513m (ν_{OH}), 2954m, 2926m, 2882w, 2854m, 1591m, 1570w, 1487w, 1469w, 1460w, 1436m-sh, 1427s, 1389w, 1361w, 1325s, 1278s, 1253s, 1238m-sh, 1223w, 1190m-sh, 1177m, 1120s, 1096m, 1070s, 1006m, 939w, 830s, 821s, 807s, 774s, 760s, 723m, 687s, 654w. ^{1}H NMR (CDCl$_3$): δ/ppm = 7.55 (dd, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, C5-H), 7.39 (dt, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, C7-H), 7.10 (t, $^3J_{HH}$ = 7.2 Hz, 1H, C6-H), 6.80 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C8-H), 5.02 (s, 1H, OH), 1.12 (s, 9H, C1-H), 0.53 (s, 6H, C3-H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ/ppm = 160.5 (C9), 136.8 (C5), 130.7 (C7), 122.7 (C4), 120.3 (C6), 115.0 (C8), 27.1 (C1), 17.8 (C2), -4.5 (C3). ^{29}Si{^{1}H} NMR (CDCl$_3$): δ/ppm = 3.2.

Hydrolysis of Ph$_2$P(O(2-C$_6$H$_4$SiMe$_2$^{t}Bu)) was also observed upon exposure of the solid to air for 24 hours, affording Ph$_2$P(O(2-C$_6$H$_4$SiMe$_2$^{t}Bu)) along with other products not including Ph$_2$PO$_2$H.

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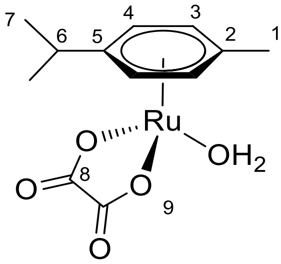
[7] (a) M. Fukui, T. Ikeda and T. Oishi, *Chem. Pharm. Bull.*, 1983, **31**, 466-475; (b) K I. O'Connor, S.-J. Wey and C. J. Burrows, *Tetrahedron Lett.*, 1992, **33**, 1001-1004.

Synthesis and characterization of [Ru(C_2O_4)(η^6-*p*-cymene)(H_2O)].[8]

Chart 6S. Structure of [Ru(C_2O_4)(η^6-*p*-cymene)(H_2O)] (numbering refers to carbon atoms).



Step 1. A solution of $AgNO_3$ (706 mg, 4.16 mmol) in H_2O (2 mL) was added dropwise to a solution of $Na_2C_2O_4$ (278 mg, 2.07 mmol) in H_2O (10 mL), causing the precipitation of $Ag_2C_2O_4$. The suspension was stirred at ambient temperature for 30’ under protection from the light. Therefore, the mixture was centrifuged and the solution removed from the colourless precipitate. The solid was suspended in few mL of H_2O, separated by centrifugation and directly used for the following reaction. *Step 2*. A solution of [$RuCl_2$(η^6-*p*-cymene)]$_2$ (212 mg, 0.346 mmol) in a MeOH:CH_2Cl_2 mixture (1:1 *v*/*v*, 4 mL) was added to a suspension of $Ag_2C_2O_4$ (theor. 2.07 mmol) in H_2O (10 mL). The mixture was stirred at ambient temperature for 14 hours under protection from the light. Therefore, the suspension was filtered on a small pad of celite and the precipitate was washed with H_2O until colourless. Volatiles were removed under vacuum from the yellow filtrate solution and the oily residue was dissolved in CH_2Cl_2. The title compound was obtained as a yellow solid upon filtration and solvent removal under vacuum (40 °C) and then stored under N_2. Yield: 220 mg, 93%. IR (solid state): $\tilde{\upsilon}$/cm^{-1} = 3460w-br (ν_{OH}), 3063w, 2964w, 2930w, 2874w, 1690s ($\nu_{C=O}$), 1667s ($\nu_{C=O}$), 1633s-sh, 1592s, 1566s, 1471m-sh, 1415s ($\nu_{C\text{-}O}$), 1387m ($\nu_{C\text{-}O}$), 1325w, 1263s, 1202w, 1161w, 1115w, 1091w, 1057w, 1034w, 1005w, 902w-sh, 875m, 789s, 731w, 694w, 669w. ^{1}H NMR (D_2O): δ/ppm = 5.84 (d, $^3J_{HH}$ = 6.1 Hz, 2H, C3-H/C4-H), 5.59 (d, $^3J_{HH}$ = 6.1 Hz, 2H, C3-H/C4-H), 2.86 (hept, $^3J_{HH}$ = 7.1 Hz, 1H, C6-H), 2.23 (s, 3H, C1-H), 1.31 (d, $^3J_{HH}$ = 6.9 Hz, 6H, C7-H). ^{13}C{^{1}H} NMR (D_2O): 166.9 (C8), 99.5 (C5), 97.1 (C2), 80.4 (C3/C4), 77.5 (C3/C4), 31.0 (C6), 21.8 (C7), 17.8 (C1).

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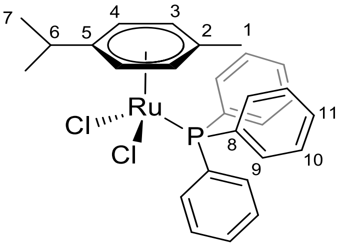
[8] W. H. Ang, E. Daldini, C. Scolaro, R. Scopelliti, L. Juillerat-Jeannerat and P. J. Dyson, *Inorg. Chem.*, 2006, **45**, 9006-9013.

Synthesis and characterization of [RuCl$_2$(η^6-*p*-cymene)(κ*P*-PPh$_3$)] (Ru-PPh$_3$).[9]

Chart 7S. Structure of **Ru-PPh$_3$** (numbering refers to carbon atoms).



In a 100-mL round bottom Schlenk flask, [RuCl$_2$(η^6-*p*-cymene)RuCl$_2$]$_2$ (218 mg, 0.356 mmol) and PPh$_3$ (234 mg, 0.892 mmol) were dissolved in CHCl$_3$ (30 mL). The brick red solution was heated under reflux for 24 hours and the progress of reaction was checked by TLC. Therefore, the reaction mixture was cooled to ambient temperature and volatiles were removed under vacuum. The brown-red residue was suspended in Et$_2$O (10 mL) with vigorous stirring. The suspension was filtered and the solid washed with Et$_2$O and dried under vacuum (40 °C). Yield: 360 mg, 89%. The compound is soluble in DMSO and chlorinated solvents, poorly soluble in Et$_2$O and insoluble in H$_2$O and hexane. Mp: dec. 142 °C (darkens). IR (solid state): $\tilde{\upsilon}$/cm^{-1} = 3048w, 2981w, 2973w, 2958w, 2925w, 2903w, 2869w, 1587w, 1573w, 1542w, 1501w, 1483m, 1470m, 1458w, 1445w-sh, 1435s, 1387m, 1376w, 1361w, 1326w, 1187w, 1159w, 1101w-sh, 1087m, 1073w, 1058m, 1035m, 1027m, 1003w, 995w-sh, 969w, 891w, 869m, 845w, 799w, 754m, 742s, 707m-sh, 693s, 674m-sh. UV-Vis (CH$_2$Cl$_2$, c = 10^{-3} M): λ_{max}/nm (ε/M^{-1}·cm^{-1}) = 375 (1.1·10^3), 478sh (6.5·10^2). ^{1}H NMR (CDCl$_3$): δ/ppm = 7.82 (pseudo-t, $^3J_{HH}$ = $^3J_{HP}$ = 8.6 Hz, 6H, C9-H), 7.41–7.31 (m, 9H, C10-H + C11-H), 5.19 (d, $^3J_{HH}$ = 4.5 Hz, 2H, C3-H/C4-H), 4.99 (d, $^3J_{HH}$ = 4.1 Hz, 2H, C3-H/C4-H), 2.84 (hept, $^3J_{HH}$ = 6.7 Hz, 1H, C6-H), 1.86 (s, 3H, C1-H), 1.09 (d, $^3J_{HH}$ = 6.7 Hz, 6H, C7-H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ/ppm = 134.3 (d, $^2J_{CP}$ = 9 Hz, C9), 133.8 (d, $^1J_{CP}$ = 46 Hz, C8), 130.2 (C11), 128.0 (d, $^3J_{CP}$ = 10 Hz, C10), 111.0 (d, $^2J_{CP}$ = 2 Hz, C5), 96.0 (C2), 89.1 (d, $^2J_{CP}$ = 3 Hz, C3/C4), 87.2 (d, $^2J_{CP}$ = 5 Hz, C3/ C4), 30.2 (C6), 21.9 (C7), 17.8 (C1). ^{31}P{^{1}H} NMR (CDCl$_3$): δ/ppm = 24.2

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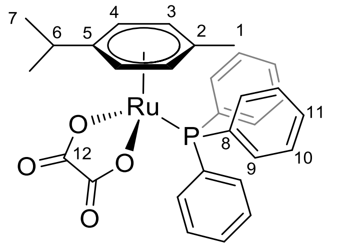
[9] E. E. Joslin, C. L. McMullin, T. B. Gunnoe, T. R. Cundari, M. Sabat and W. H. Myers, *Inorg. Chem.*, 2012, **51**, 4791-4801.

Synthesis and characterization of [Ru(C_2O_4)(η^6-*p*-cymene)(κ*P*-PPh_3)] (Ru-PPh_3-O).[10]

Chart 8S. Structure of **Ru-PPh_3-O** (numbering refers to carbon atoms).



Freshly prepared [Ru(C_2O_4)(η^6-*p*-cymene)(H_2O)] (108 mg, 0.317 mmol) and PPh_3 (84 mg, 0.320 mmol) were dissolved in CH_2Cl_2 (10 mL). The resulting yellow-orange solution was stirred at ambient temperature for 3 hours and the progress of reaction was checked by TLC. Therefore the solution was filtered, volatiles were removed under vacuum and the residue was dissolved in a small volume of CH_2Cl_2. Addition of Et_2O under vigorous stirring caused the precipitation of a yellow solid. The suspension was filtered; the solid was washed with Et_2O and dried under vacuum (40 °C). Yield: 170 mg, 91%. The title compound is soluble in DMSO, MeOH and chlorinated solvents, poorly soluble in acetone and insoluble in Et_2O, hexane and H_2O. IR (solid state): $\tilde{\upsilon}$/cm^{-1} = 3077w-sh, 3058w, 2967w, 2876w, 1688s, 1666s and 1652s ($\nu_{C=O}$), 1586w, 1573w, 1504w, 1482m, 1469m, 1434m, 1356s ($\nu_{C–O}$), 1324m-sh, 1280w, 1227w, 1187w, 1159w, 1098m, 1092m, 1056w, 1036w, 998w, 953w, 909w, 896w, 849m, 800w, 782m, 748m, 696s. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.58–7.42 (m, 15H, Ph), 5.34 (s-br, 2H, C3-H/C4-H), 5.10 (s-br, 2H, C3-H/C4-H), 2.61–2.53 (m, 1H, C6-H), 1.95 (s, 3H, C1-H), 1.19 (d, $^3J_{HH}$ = 6.3 Hz, 6H, C7-H).[11] ^{1}H NMR (CD_3OD): δ/ppm = 7.58–7.46 (m, 15H, Ph), 5.72 (d, $^3J_{HH}$ = 5.6 Hz, 2H, C3-H/C4-H), 5.40 (d, $^3J_{HH}$ = 5.3 Hz, 2H, C3-H/C4-H), 2.59 (hept, $^3J_{HH}$ = 6.5 Hz, 1H, C6-H), 1.93 (s, 3H, C1-H), 1.22 (d, $^3J_{HH}$ = 6.7 Hz, 6H, C7-H). ^{13}C{^{1}H} NMR (CD_3OD): δ/ppm = 167.1 (C12), 135.4 (d, $^2J_{CP}$ = 10 Hz, C9), 132.4 (d, $^4J_{CP}$ = 2.1 Hz, C11), 130.7 (d, $^1J_{CP}$ = 46.1 Hz, C8), 130.0 (d, $^3J_{CP}$ = 10.3 Hz, C10), 108.9 (d, $^2J_{CP}$ = 2.9 Hz, C5), 99.2 (C2), 89.2 (d, $^2J_{CP}$ = 4.0 Hz, C3/C4), 88.0 (d, $^2J_{CP}$ = 2.9 Hz, C3/C4), 32.2 (C6), 22.4 (C7), 18.0 (C1). ^{31}P{^{1}H} NMR ($CDCl_3$): δ/ppm = 29.8. ^{31}P{^{1}H} NMR (CD_3OD): δ/ppm = 31.9.

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[10] H. Yan, G. Süss-Fink, A. Neels and H. Stoeckli-Evans, *J. Chem. Soc., Dalton Trans.*, 1997, 4345–4350.

[11] The compound is not stable if maintained in $CDCl_3$ for > 1 h (see later “Stability studies in chloroform solutions”)

Figure 1S. IR spectrum of [RuCl$_2$(η^6-*p*-cymene){κP-Ph$_2$P(4-C$_6$H$_4$OSiMe$_2{}^t$Bu)}], **1**.

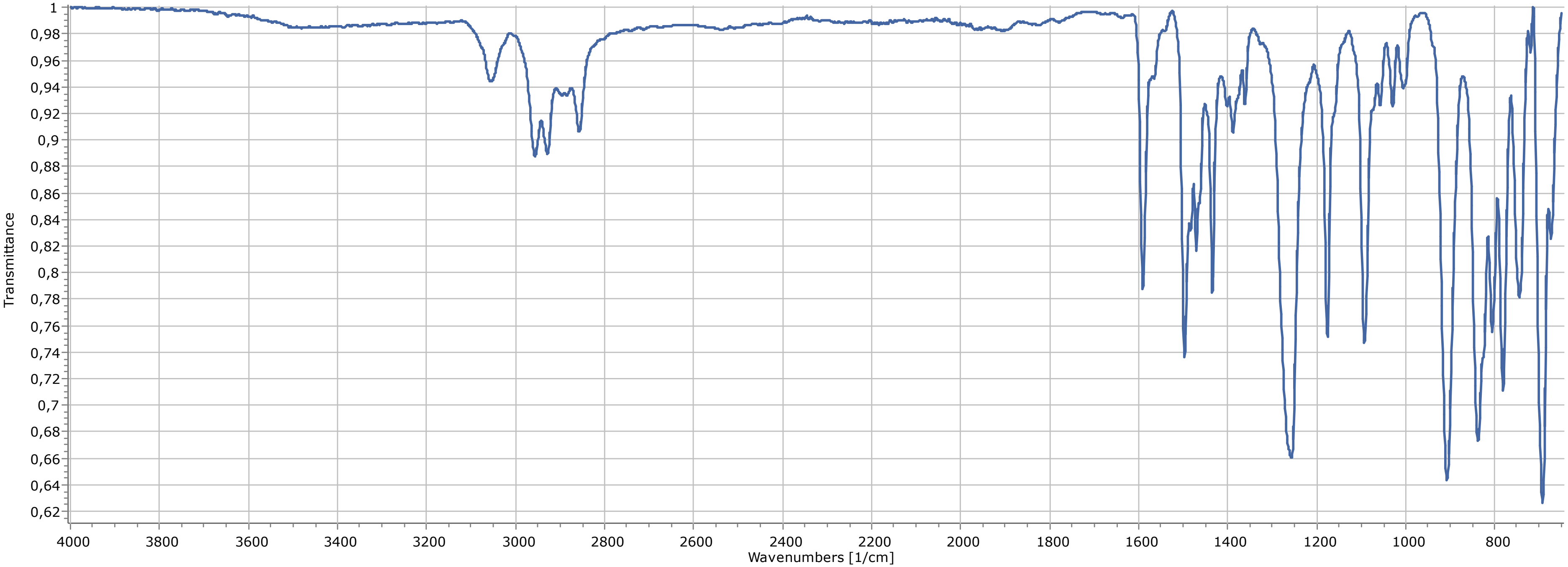


Figure 2S. IR spectrum of $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{\kappa P\text{-}Ph_2P(4\text{-}C_6H_4Br)\}]$, **2**.

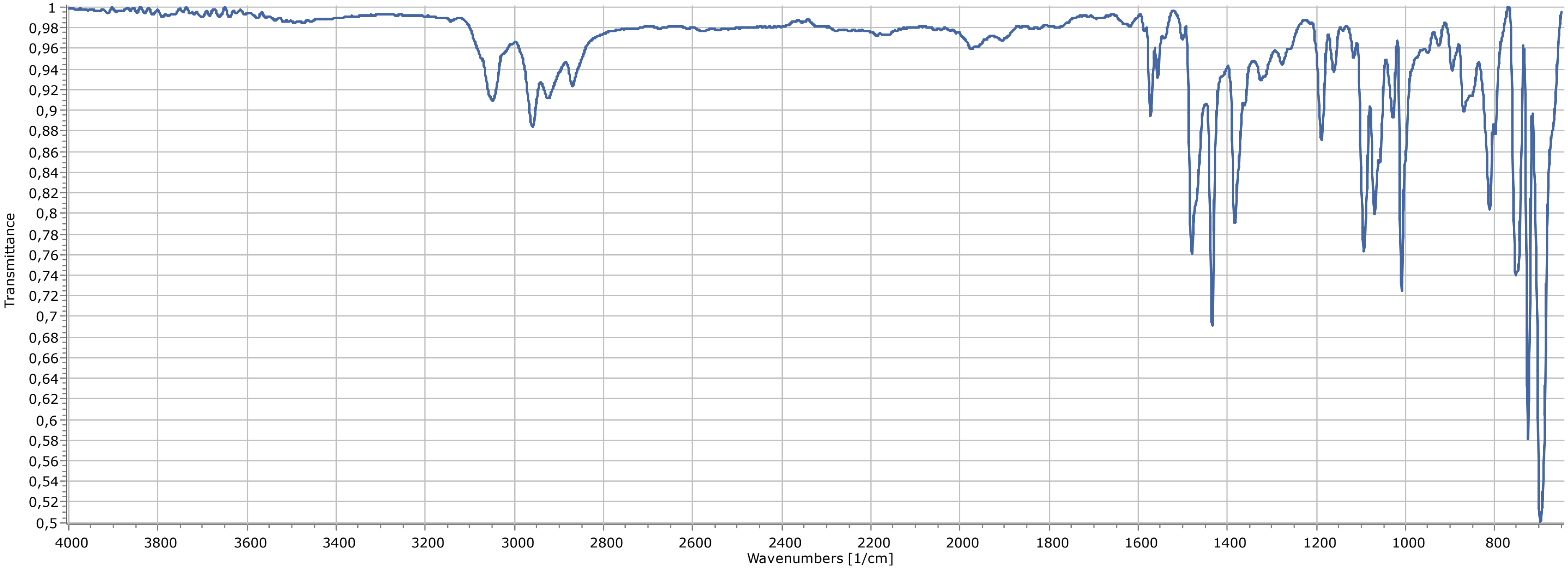


Figure 3S. IR spectrum of [$RuCl_2$(η^6-*p*-cymene){κ*P*-$Ph_2P(4-C_6H_4OCOCHCl_2)$}], **3**.

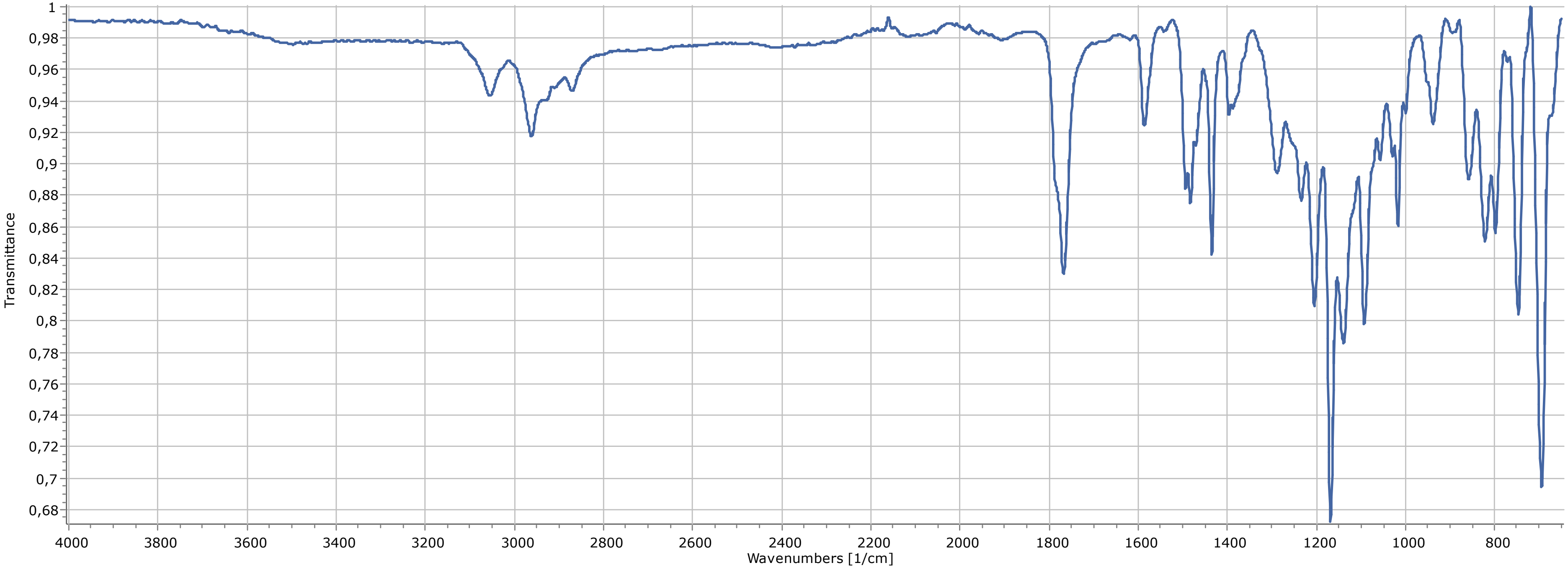


Figure 4S. IR spectrum of [RuCl$_2$(η^6-*p*-cymene)(κP-Ph$_2$POPh)], **4**.

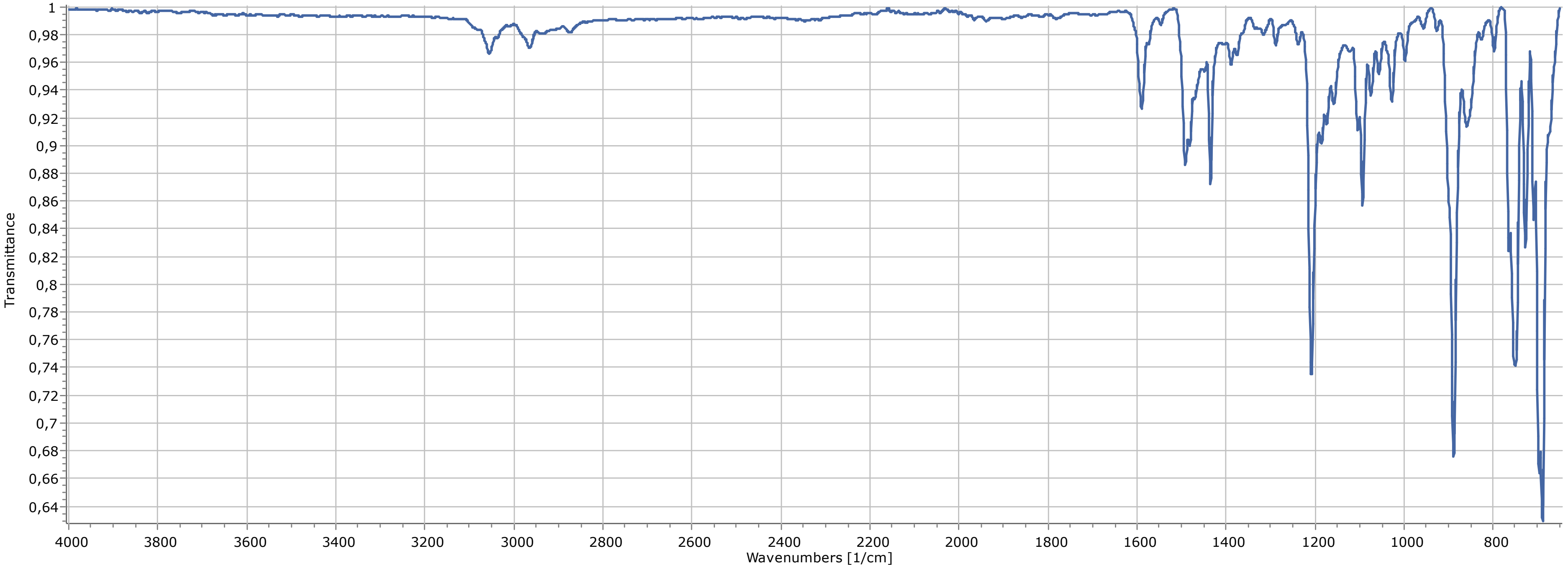


Figure 5S. IR spectrum of [RuCl$_2$(η^6-*p*-cymene){κ*P*-Ph$_2$PO(2-C$_6$H$_4$(SiMe$_2$^{t}Bu))}], **5**.

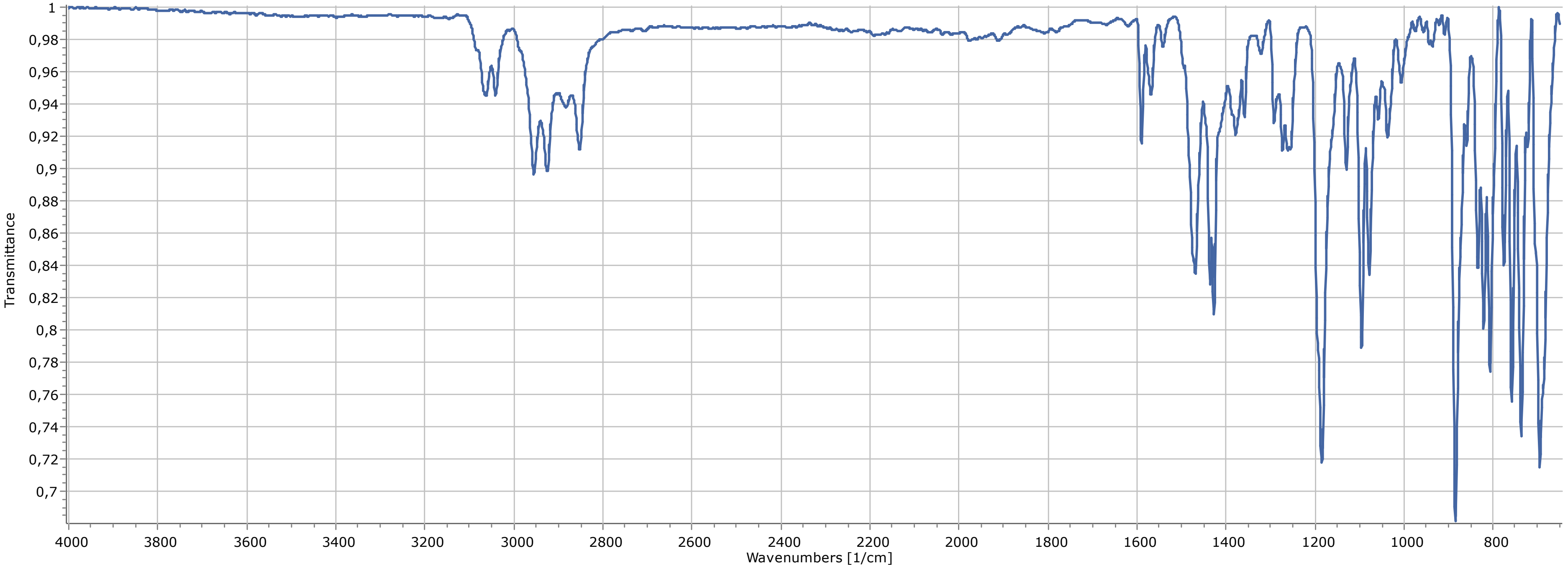


Figure 6S. IR spectrum of [Ru(C_2O_4)(η^6-*p*-cymene){κ*P*-$Ph_2PO(2\text{-}C_6H_4(SiMe_2{}^tBu))$}], **6**.

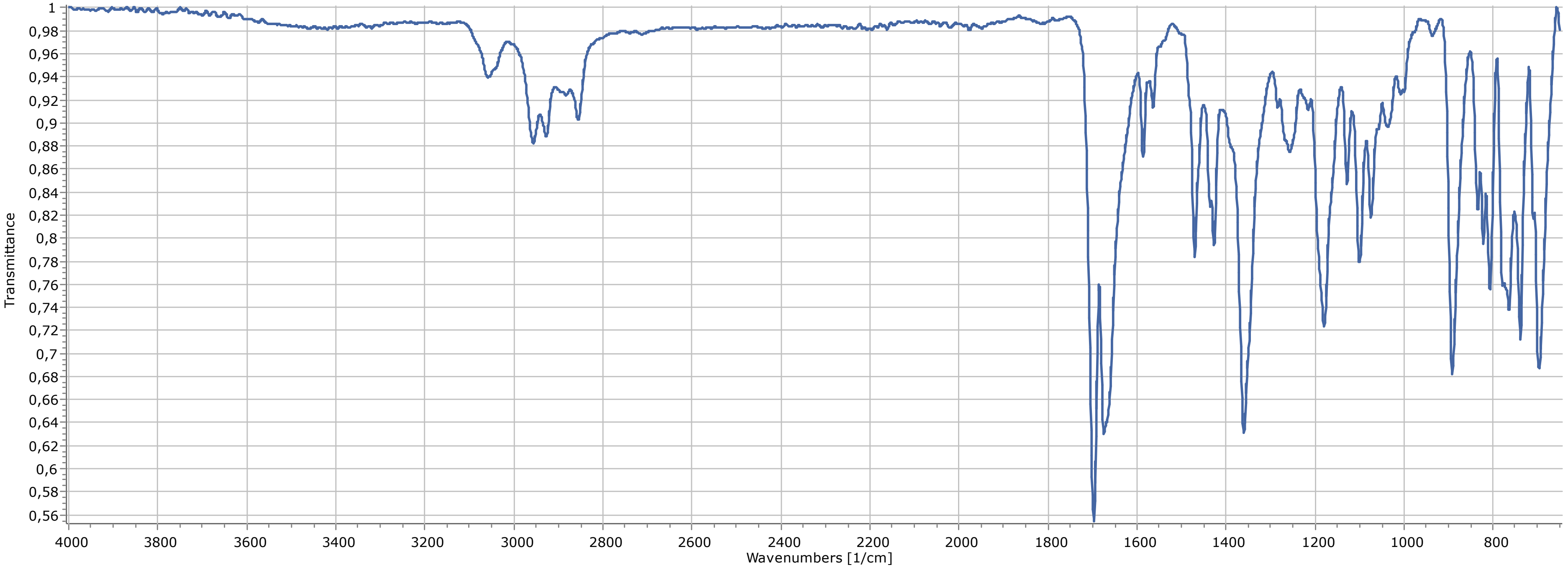


Figure 7S. IR spectrum of [$RuCl_2$(η^6-*p*-cymene)(κ*P*-PPh_3)], **Ru-PPh$_3$**.

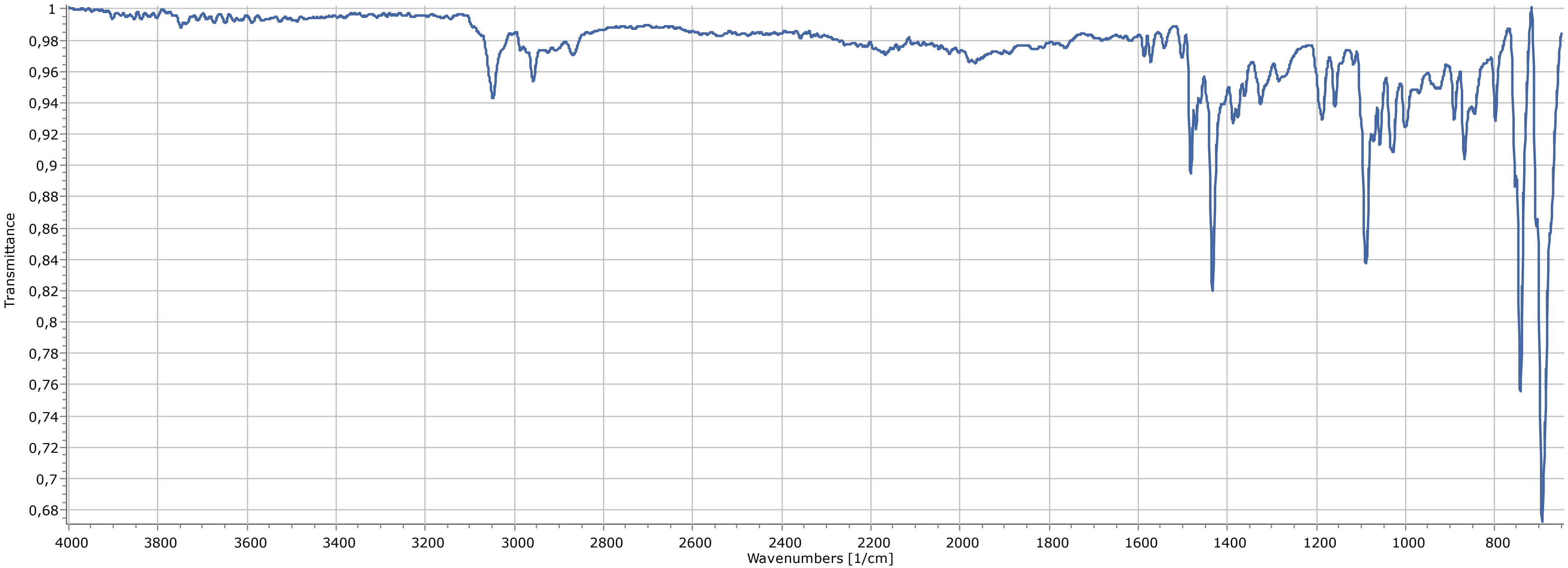


Figure 8S. IR spectrum of [Ru(C_2O_4)(η^6-*p*-cymene)(κP-PPh_3)], **Ru-PPh$_3$-O**.

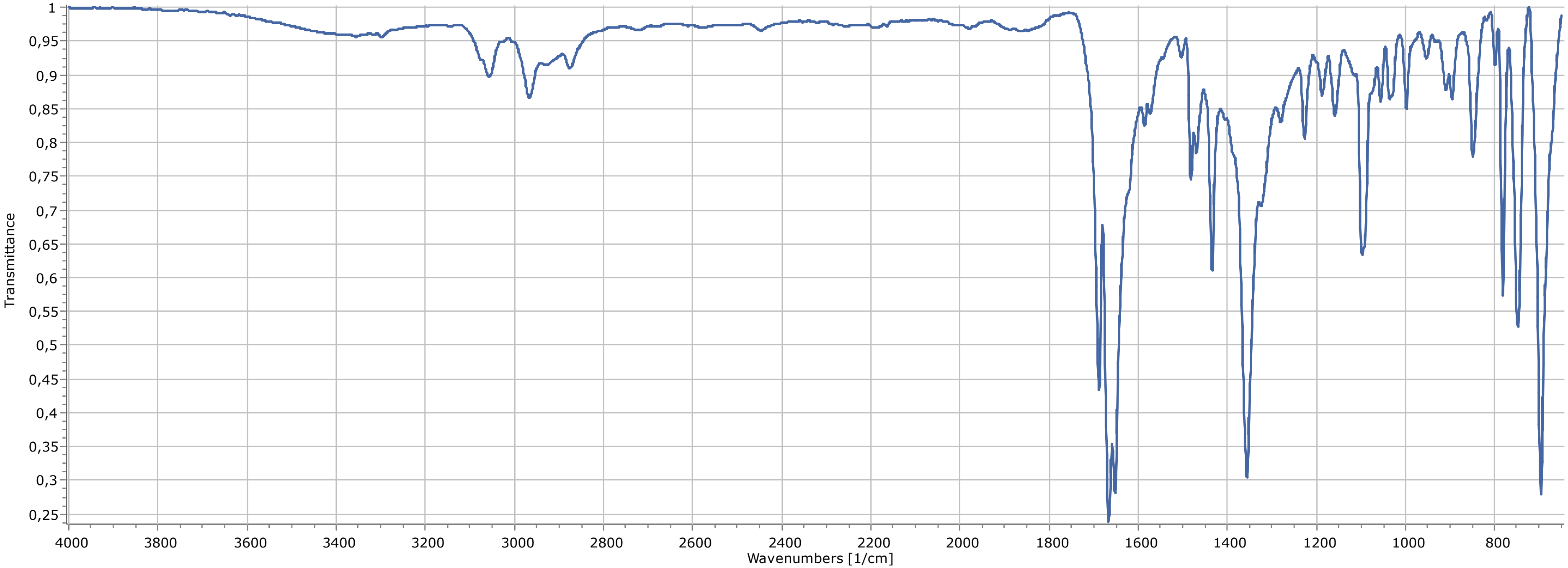


Figure 9S. ^{1}H NMR spectrum of [RuCl$_2$(η^6-*p*-cymene){κ*P*-Ph$_2$P(4-C$_6$H$_4$OSiMe$_2$^{t}Bu)}], **1**, in CDCl$_3$.

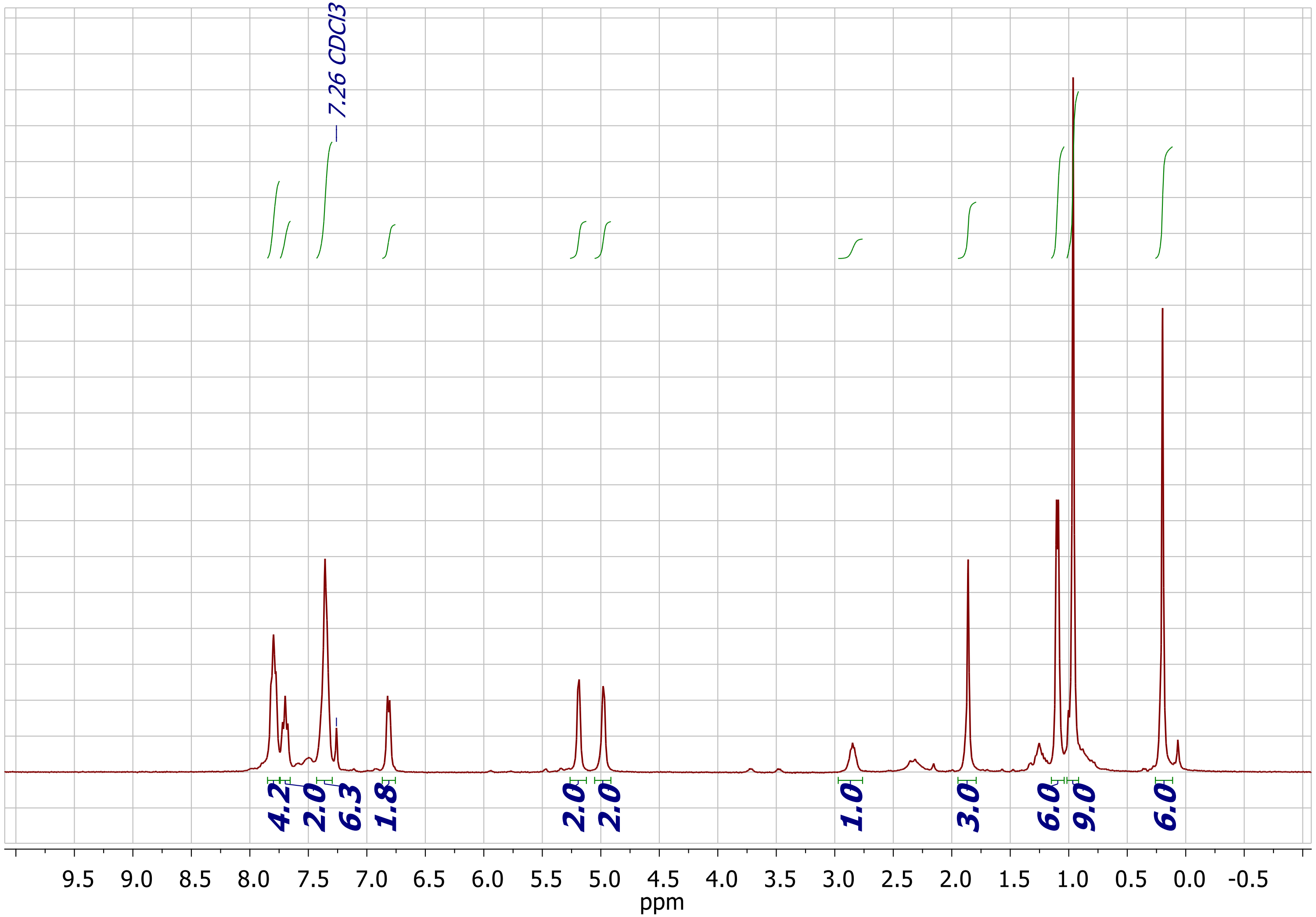
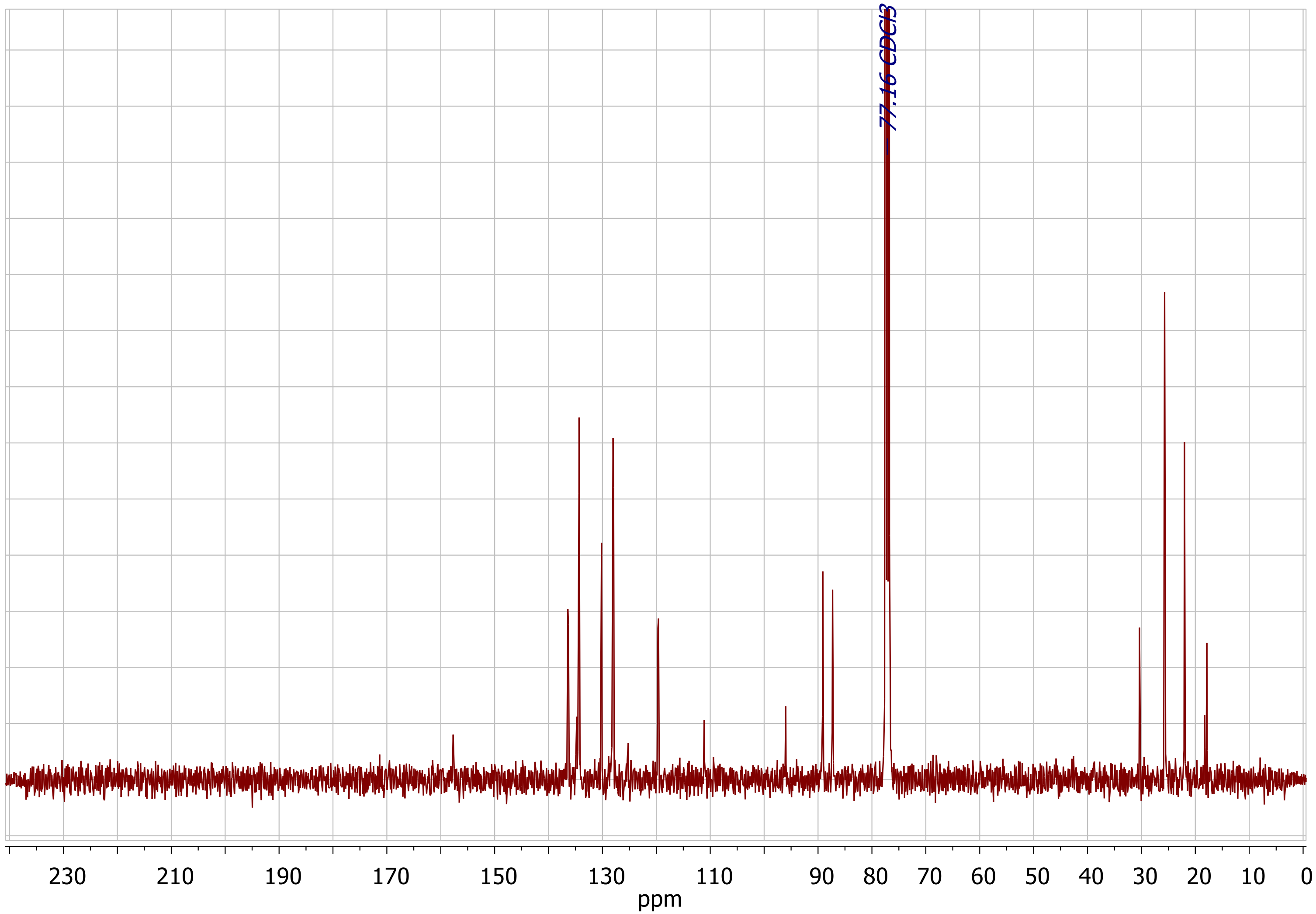


Figure 10S. $^{13}C\{^1H\}$ NMR spectrum of [$RuCl_2$(η^6-*p*-cymene){κ*P*-Ph_2P(4-$C_6H_4OSiMe_2{}^tBu$)}], **1**, in $CDCl_3$.



The signal for the Si-CH_3 group (-4.5 ppm) falls out of the range of this spectrum and was identified via HMBC.

Figure 11S. $^{29}Si\{^1H\}$ NMR spectrum of $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{\kappa P\text{-}Ph_2P(4\text{-}C_6H_4OSiMe_2{}^tBu)\}]$, **1**, in $CDCl_3$.

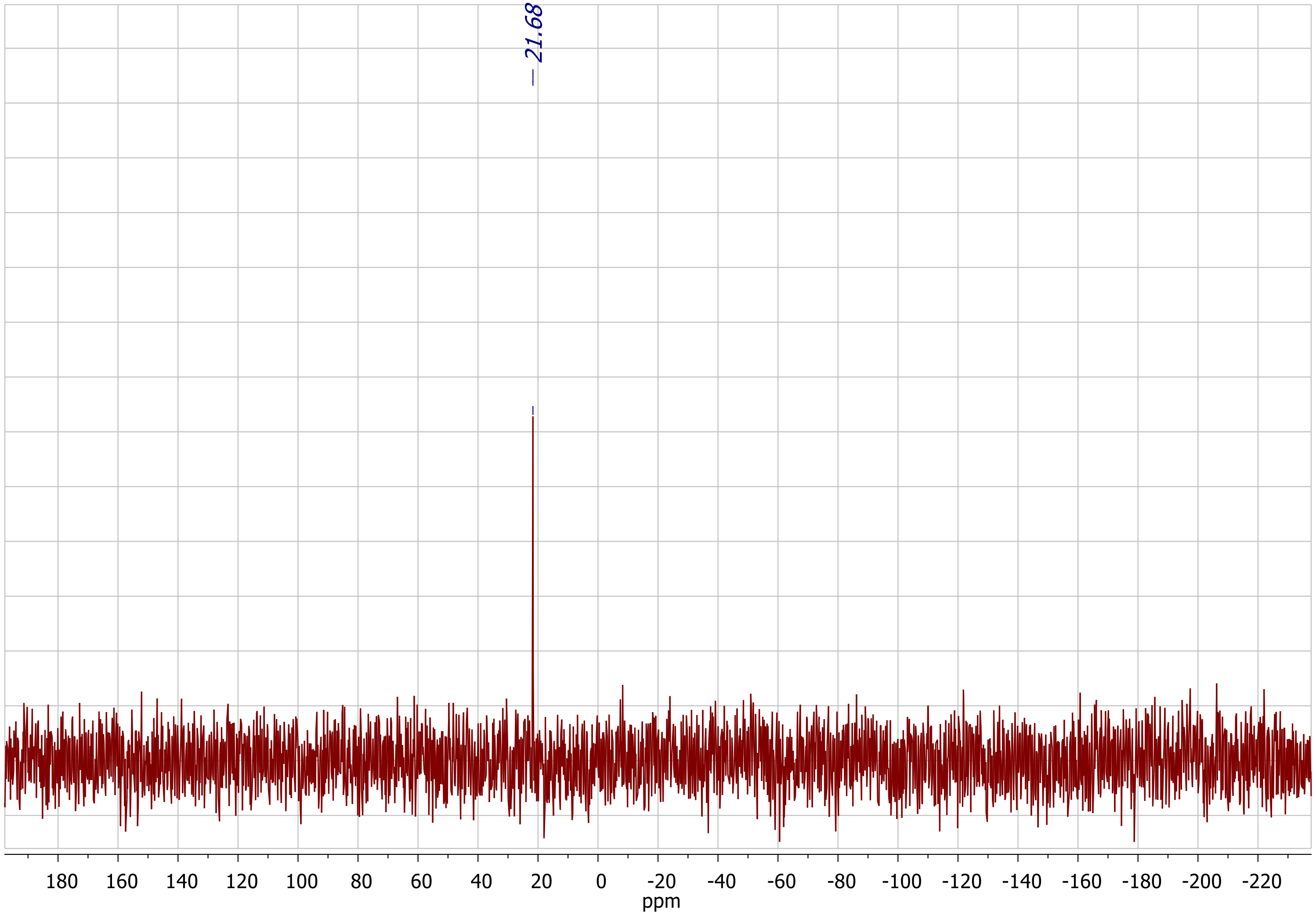


Figure 12S. $^{31}P\{^1H\}$ NMR spectrum of $[RuCl_2(\eta^6$-*p*-cymene$)\{\kappa P$-$Ph_2P(4$-$C_6H_4OSiMe_2{}^tBu)\}]$, **1**, in $CDCl_3$.

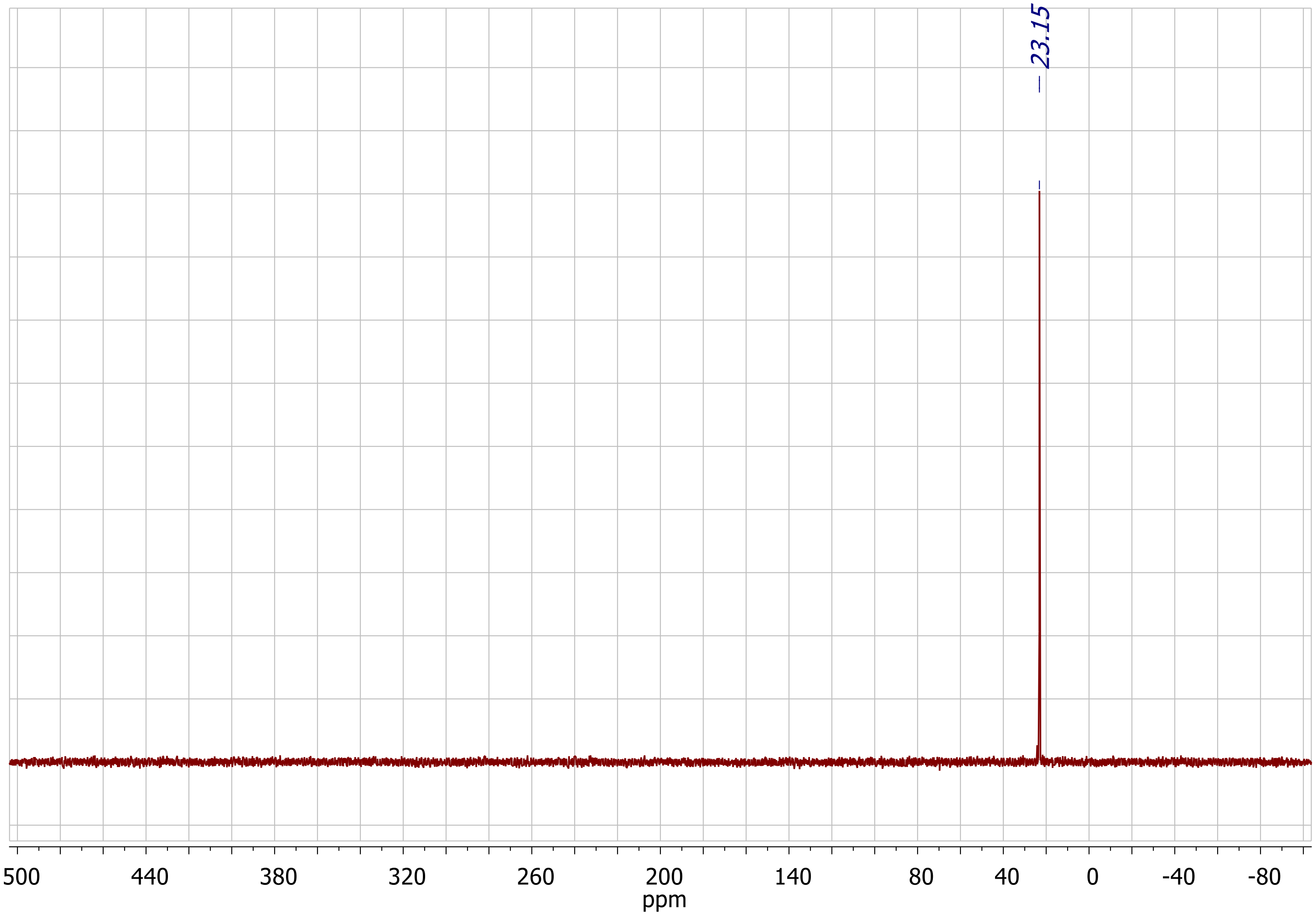


Figure 13S. ^{1}H NMR spectrum of [RuCl$_2$(η^6-*p*-cymene){κ*P*-Ph$_2$P(4-C$_6$H$_4$Br)}], **2**, in CDCl$_3$.

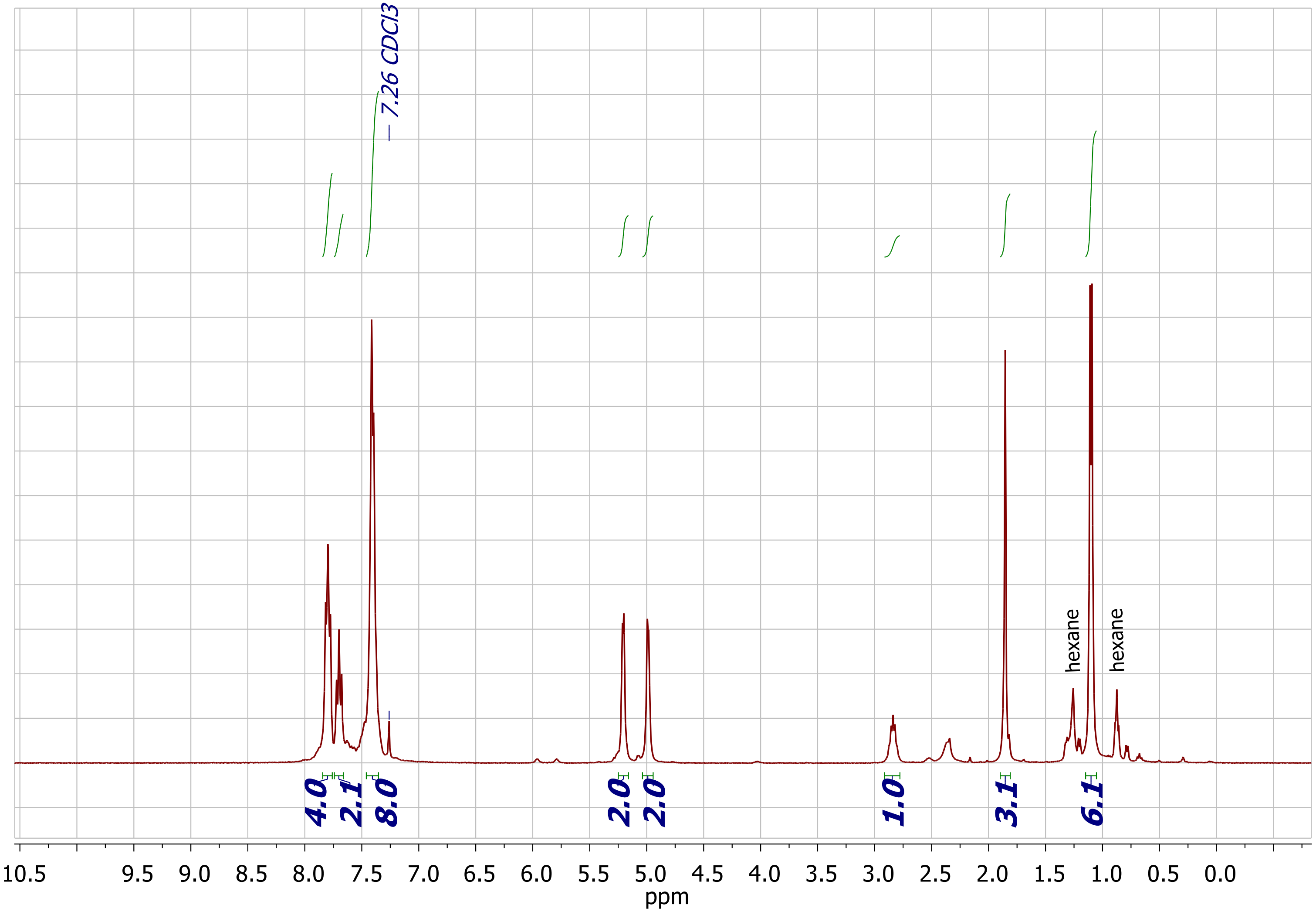


Figure 14S. $^{13}C\{^{1}H\}$ NMR spectrum of [$RuCl_2$(η^6-*p*-cymene){κ*P*-$Ph_2P(4\text{-}C_6H_4Br)$}], **2**, in $CDCl_3$.

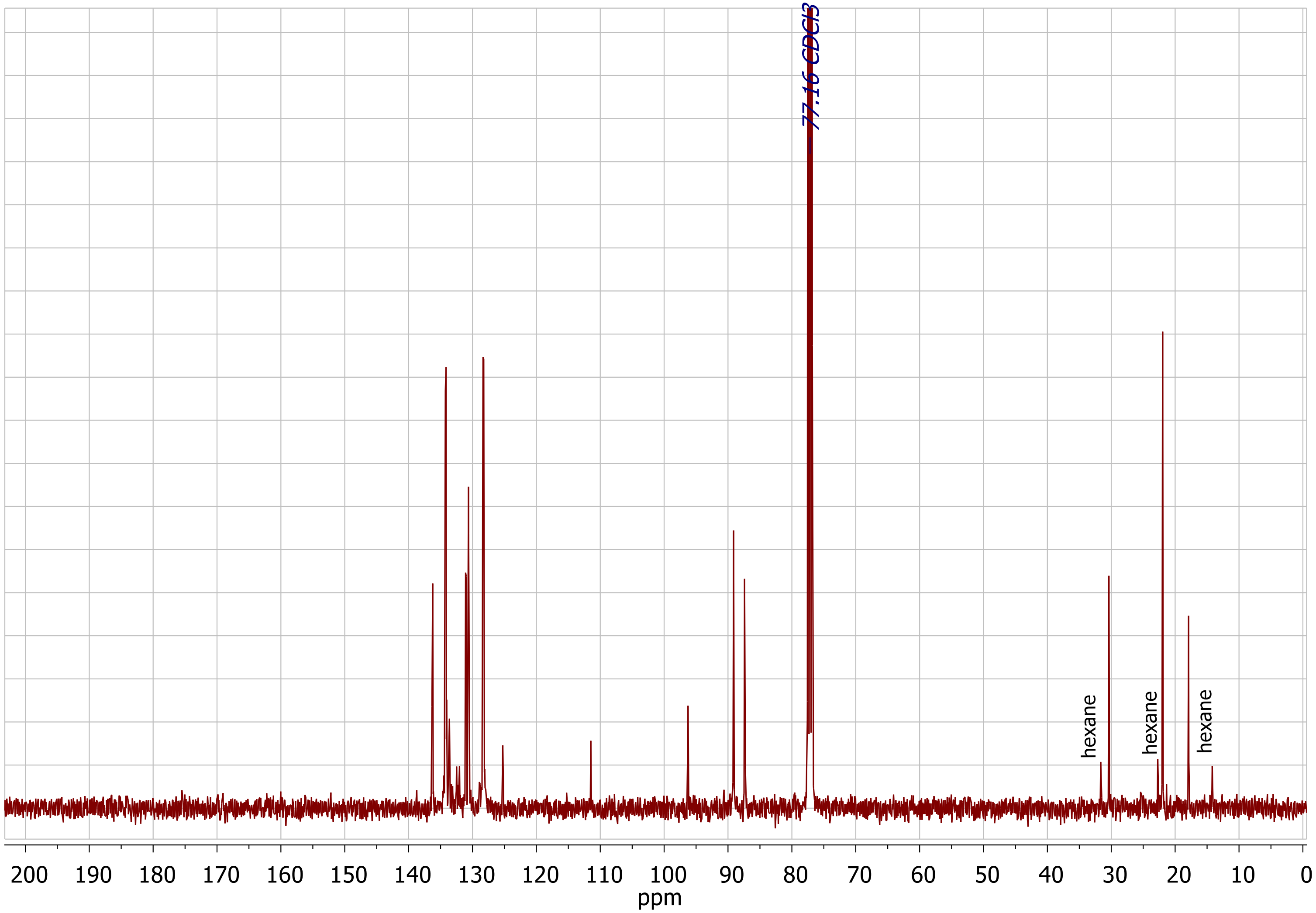


Figure 15S. $^{31}P\{^{1}H\}$ NMR spectrum of [RuCl$_2$(η^6-*p*-cymene){κ*P*-Ph$_2$P(4-C$_6$H$_4$Br)}], **2**, in CDCl$_3$.

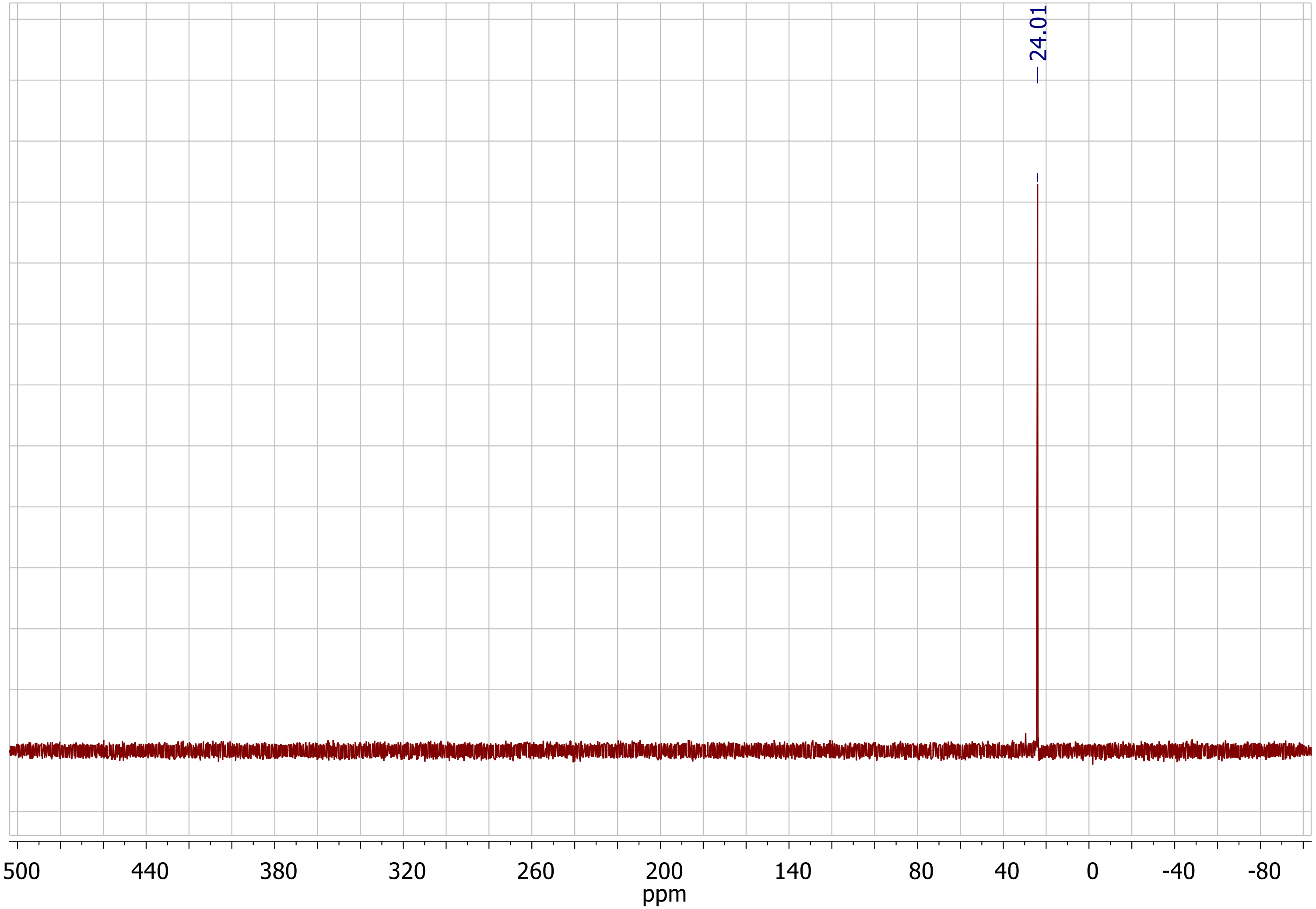


Figure 16S. ^{1}H NMR spectrum of [RuCl$_2$(η^6-*p*-cymene){κ*P*-Ph$_2$P(4-C$_6$H$_4$OCOCHCl$_2$)}], **3**, in CDCl$_3$.

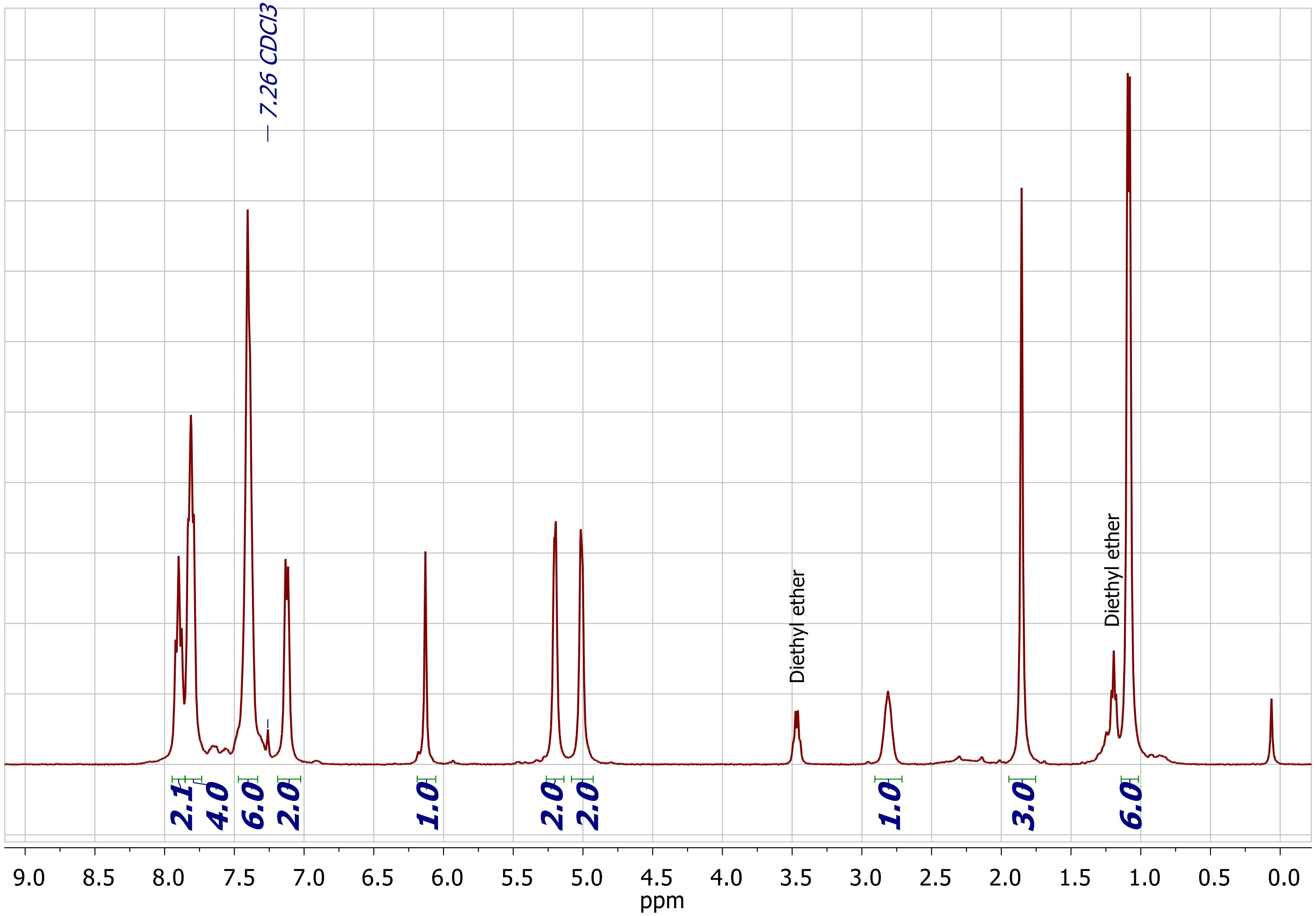


Figure 17S. $^{13}C\{^1H\}$ NMR spectrum of [RuCl$_2$(η^6-*p*-cymene){κ*P*-Ph$_2$P(4-C$_6$H$_4$OCOCHCl$_2$)}], **3**, in CDCl$_3$.

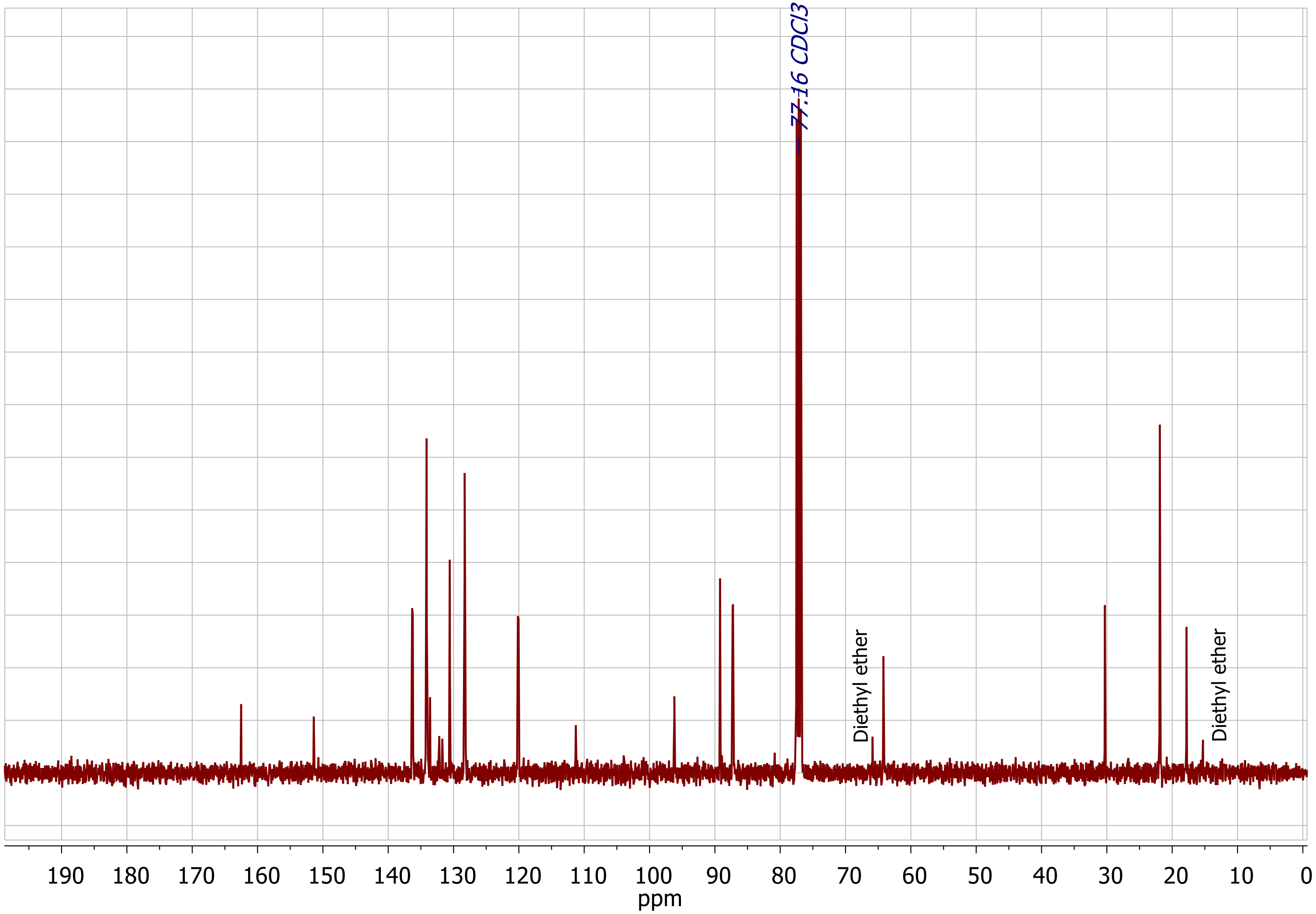


Figure 18S. $^{31}P\{^{1}H\}$ NMR spectrum of $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{\kappa P\text{-}Ph_2P(4\text{-}C_6H_4OCOCHCl_2)\}]$, **3**, in $CDCl_3$.

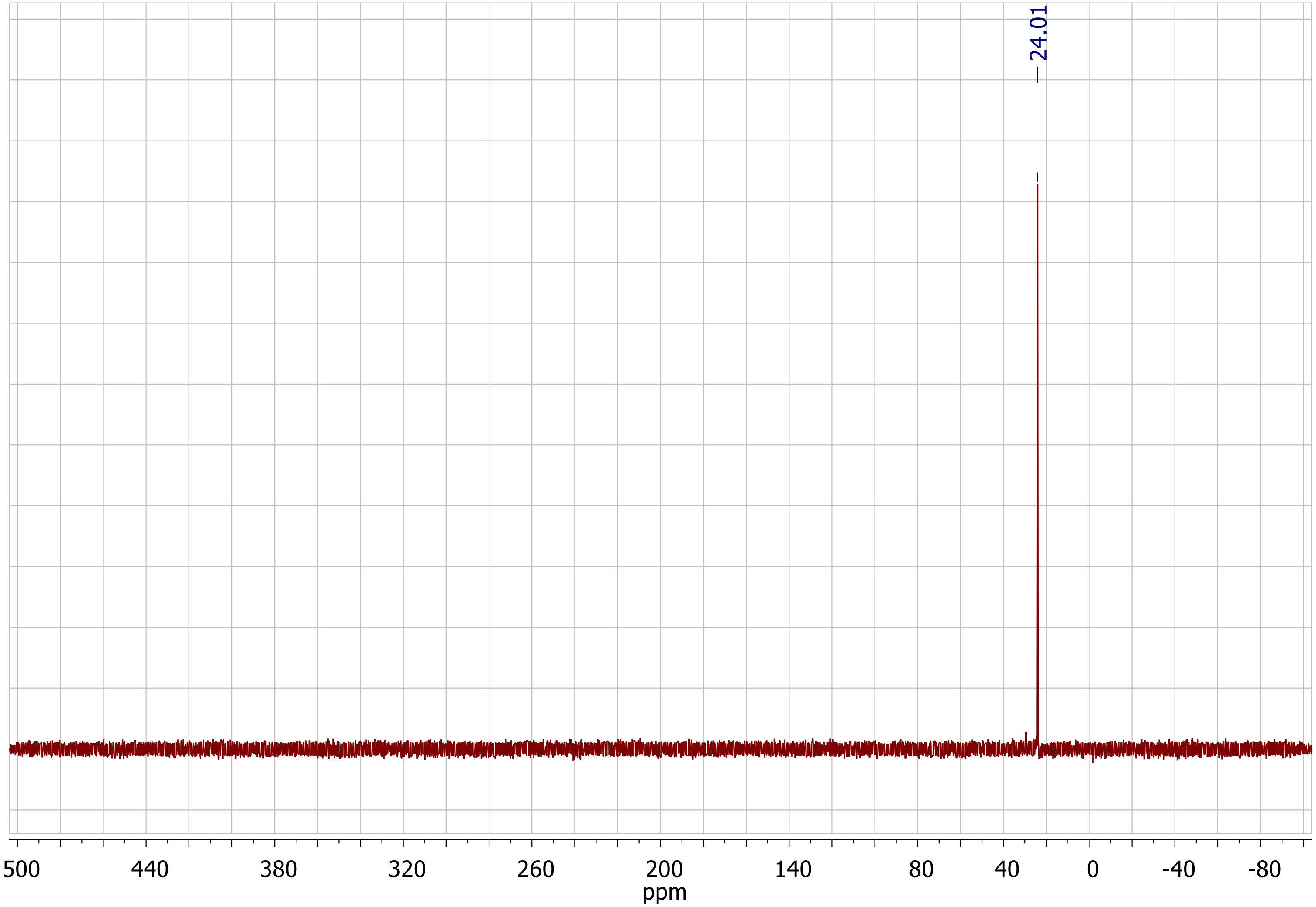


Figure 19S. ^{1}H NMR spectrum of [RuCl$_2$(η^6-*p*-cymene)(κ*P*-Ph$_2$POPh)], **4**, in CDCl$_3$.

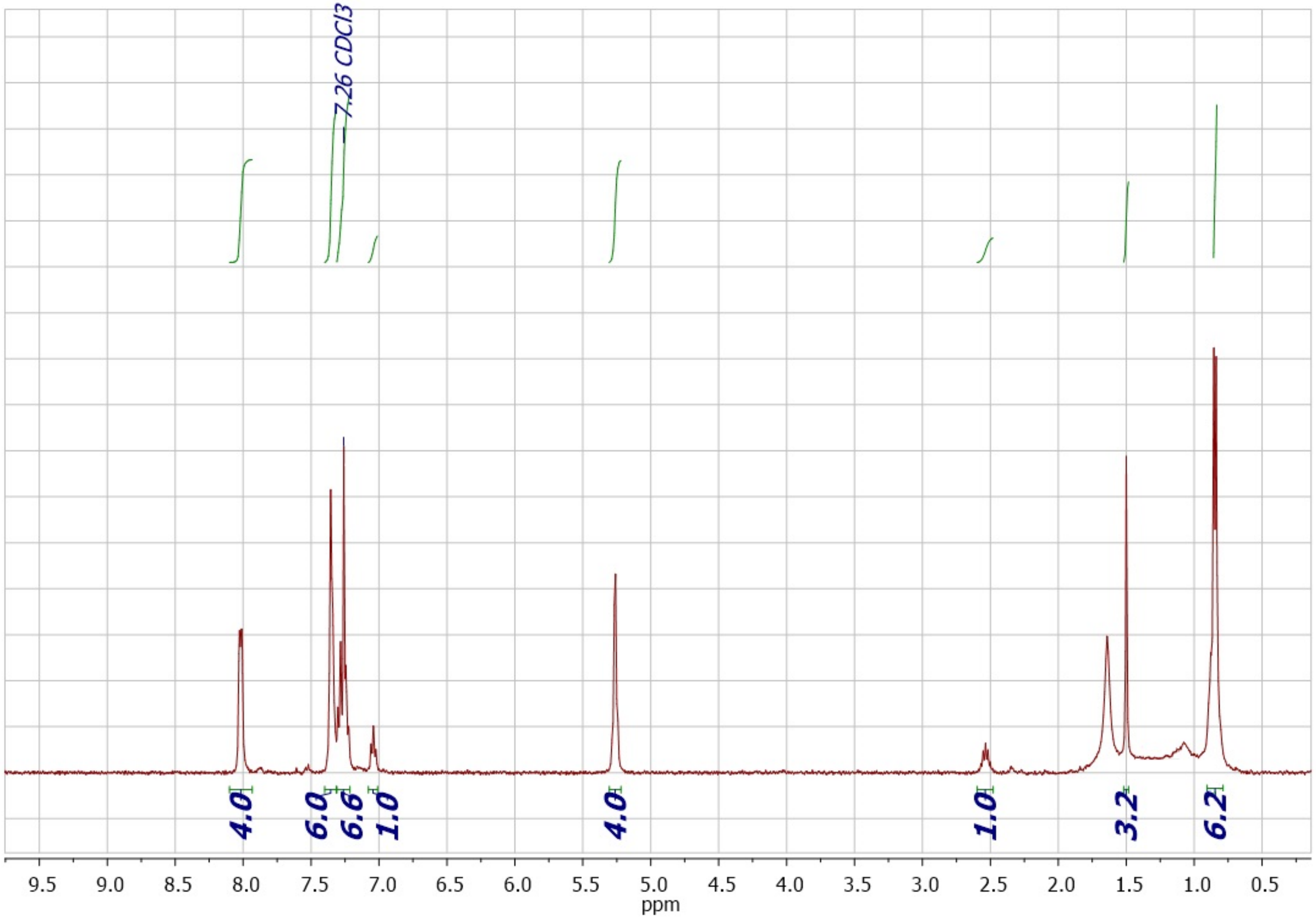


Figure 20S. $^{13}C\{^{1}H\}$ NMR spectrum of $[RuCl_2(\eta^6\text{-}p\text{-cymene})(\kappa P\text{-}Ph_2POPh)]$, **4**, in $CDCl_3$.

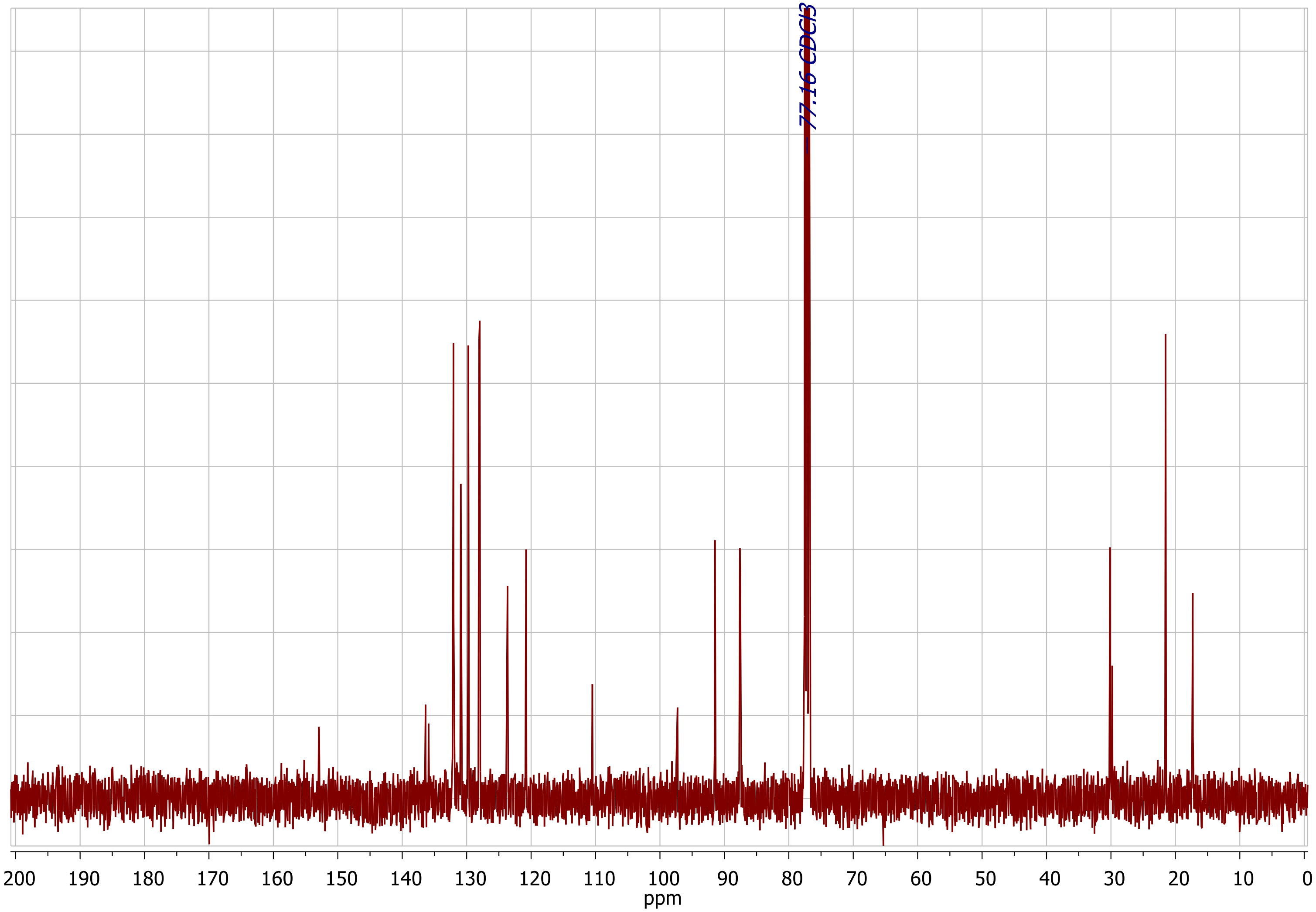


Figure 21S. $^{31}P\{^1H\}$ NMR spectrum of [RuCl$_2$(η^6-*p*-cymene)(κ*P*-Ph$_2$POPh)], **4**, in CDCl$_3$.

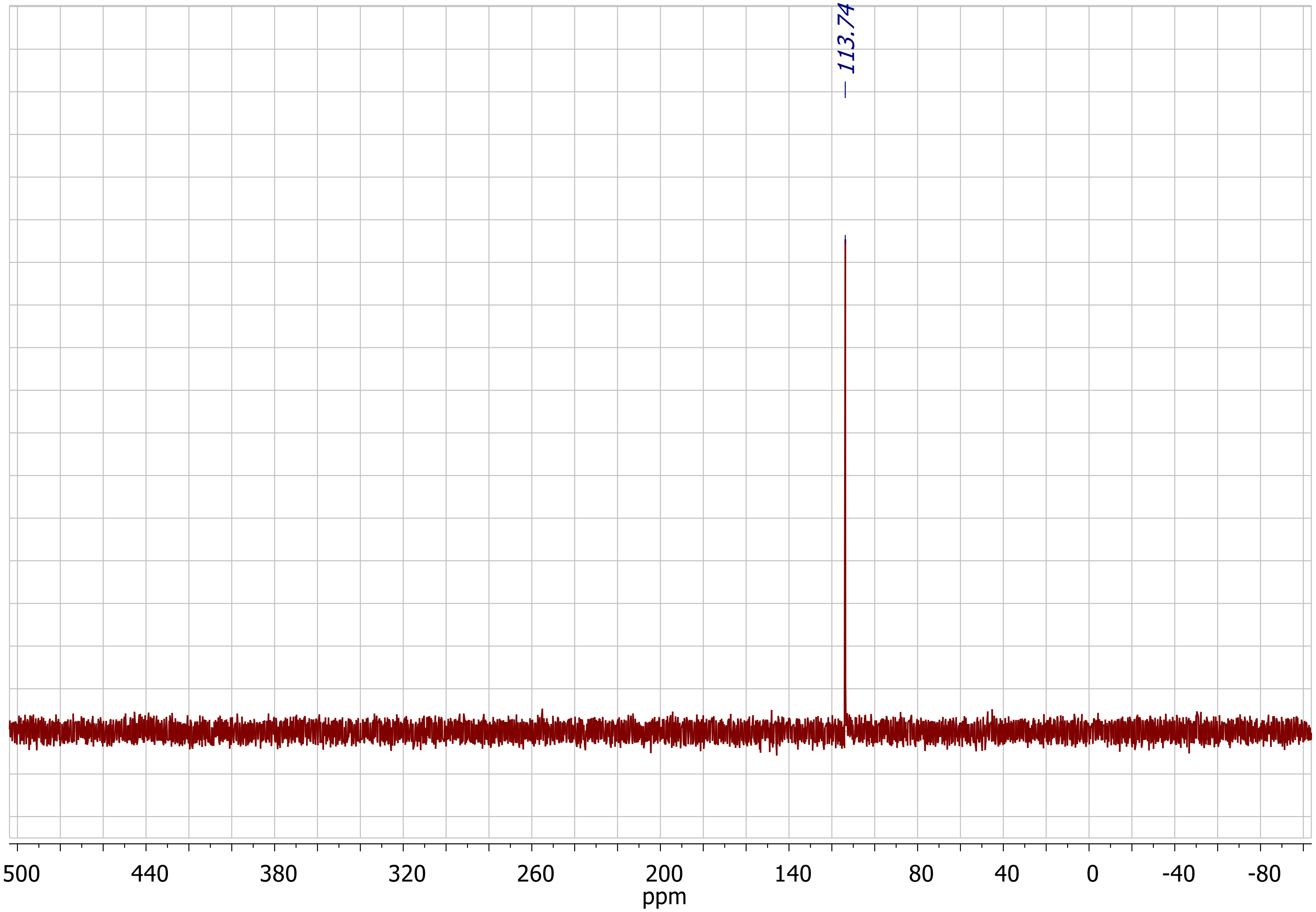


Figure 22S. ^{1}H NMR spectrum of $[\mathrm{RuCl_2}(\eta^6\text{-}p\text{-cymene})\{\kappa P\text{-}\mathrm{Ph_2PO(2\text{-}C_6H_4(SiMe_2{}^tBu))}\}]$, **5**, in $\mathrm{CDCl_3}$.

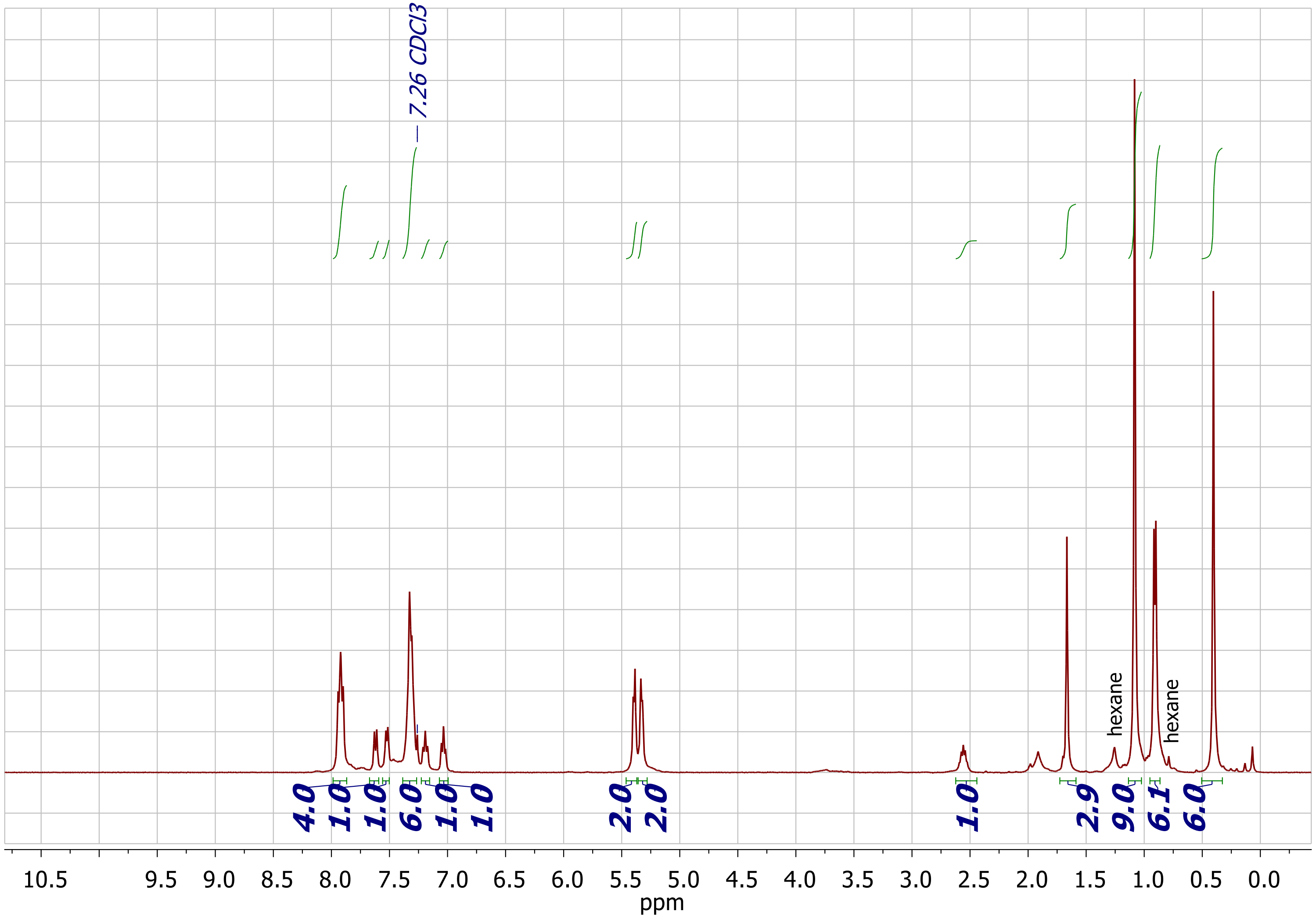


Figure 23S. $^{13}C\{^1H\}$ NMR spectrum of $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{\kappa P\text{-}Ph_2PO(2\text{-}C_6H_4(SiMe_2{}^tBu))\}]$, **5**, in $CDCl_3$.

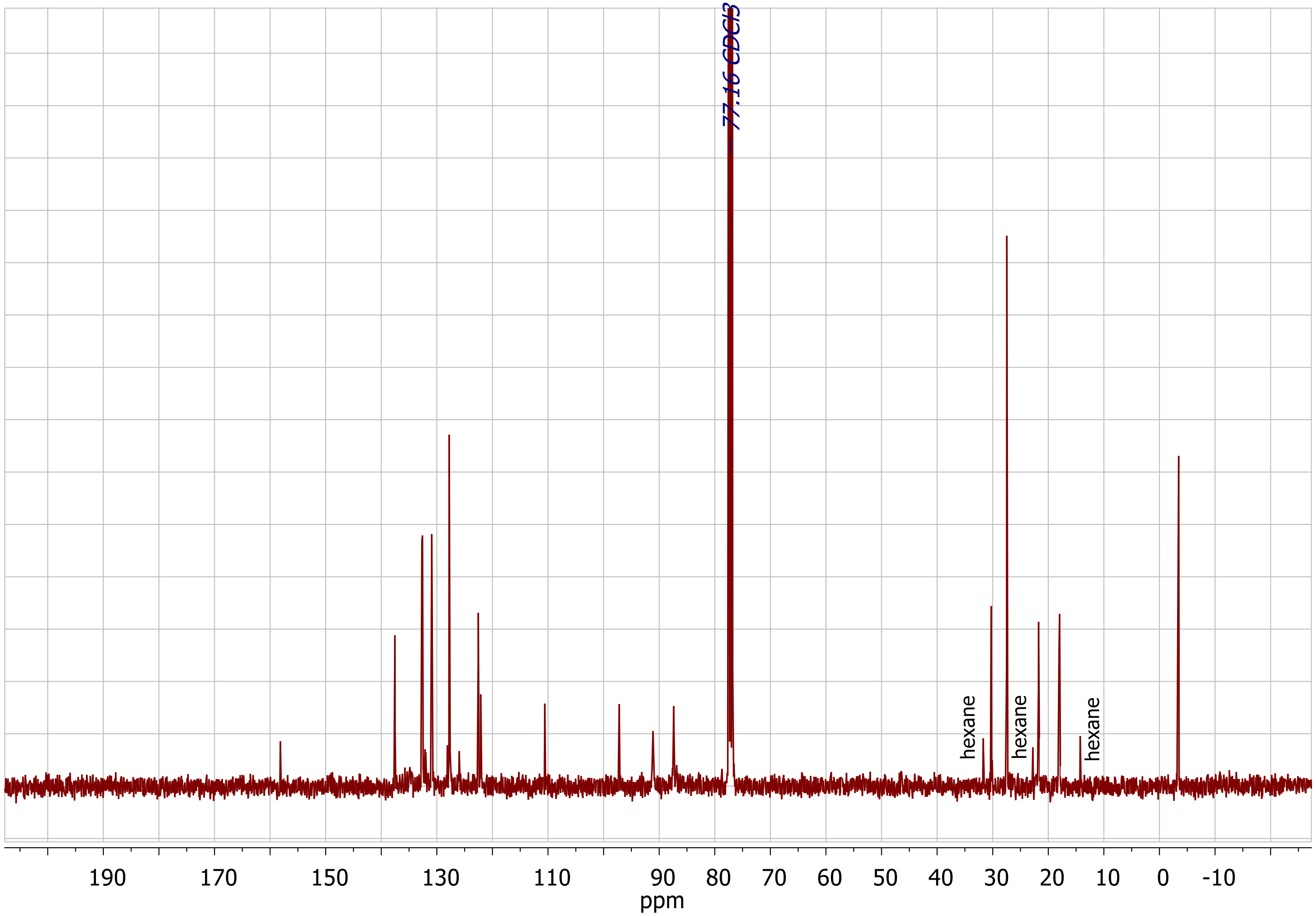


Figure 24S. $^{29}Si\{^1H\}$ NMR spectrum of $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{\kappa P\text{-}Ph_2PO(2\text{-}C_6H_4(SiMe_2{}^tBu))\}]$, **5**, in $CDCl_3$.

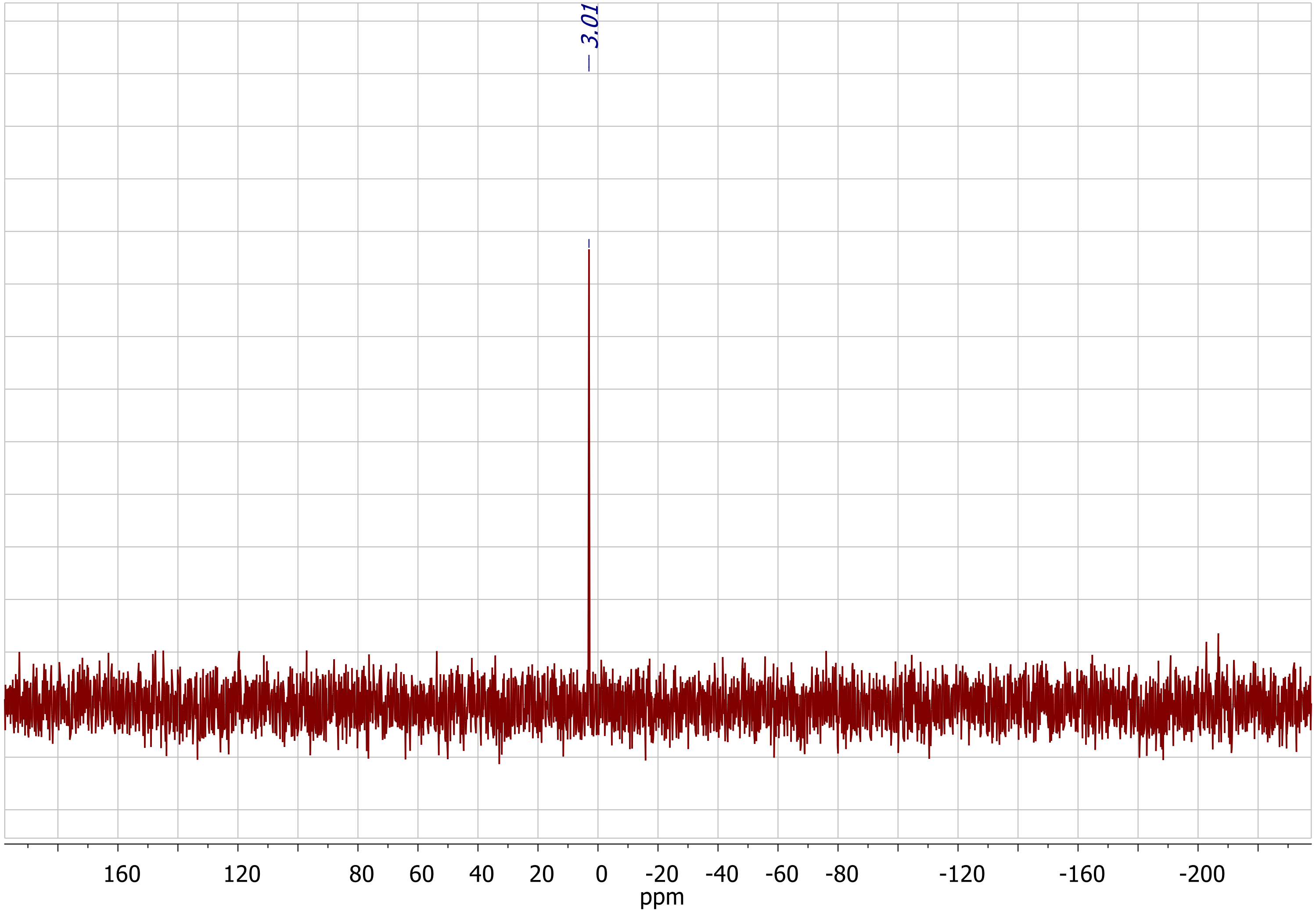


Figure 25S. $^{31}P\{^{1}H\}$ NMR spectrum of $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{\kappa P\text{-}Ph_2PO(2\text{-}C_6H_4(SiMe_2{}^tBu))\}]$, **5**, in $CDCl_3$.

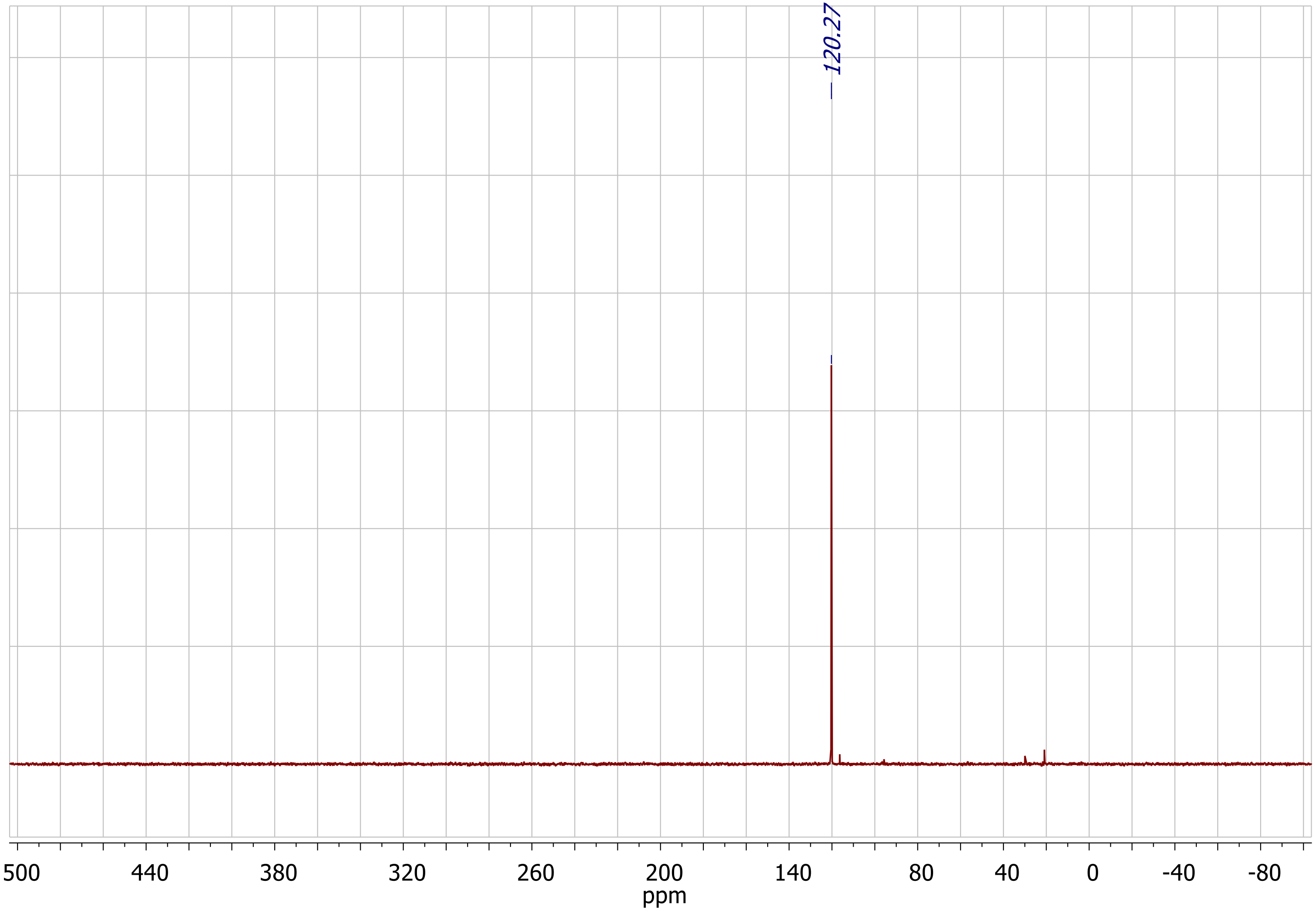


Figure 26S. ^{1}H NMR spectrum of [Ru(C_2O_4)(η^6-*p*-cymene){κ*P*-$Ph_2PO(2-C_6H_4(SiMe_2{}^tBu))$}], **6**, in $CDCl_3$.

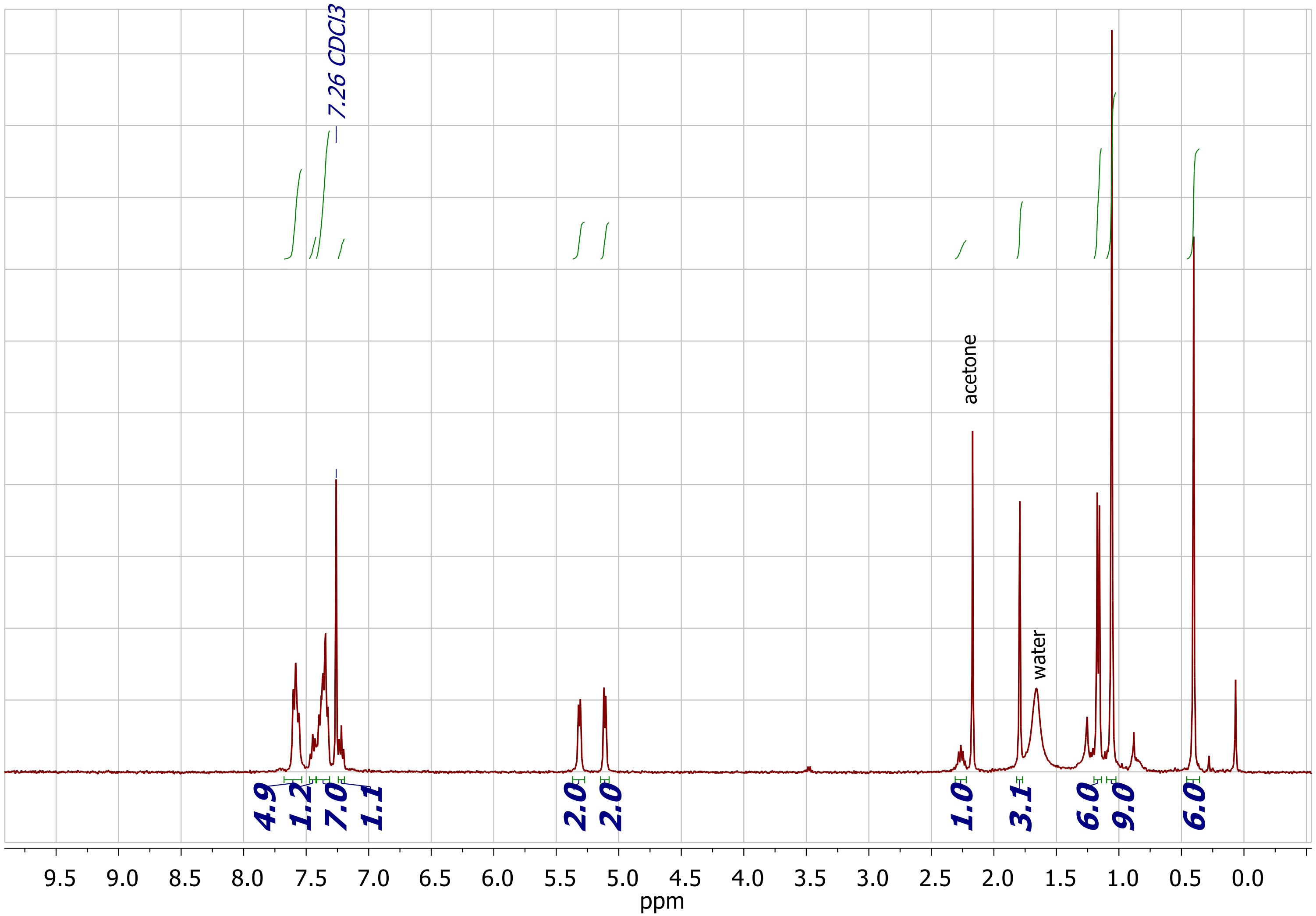


Figure 27S. $^{13}C\{^1H\}$ NMR spectrum of [Ru(C_2O_4)(η^6-*p*-cymene){κ*P*-$Ph_2PO(2\text{-}C_6H_4(SiMe_2{}^tBu))$}], **6**, in $CDCl_3$.

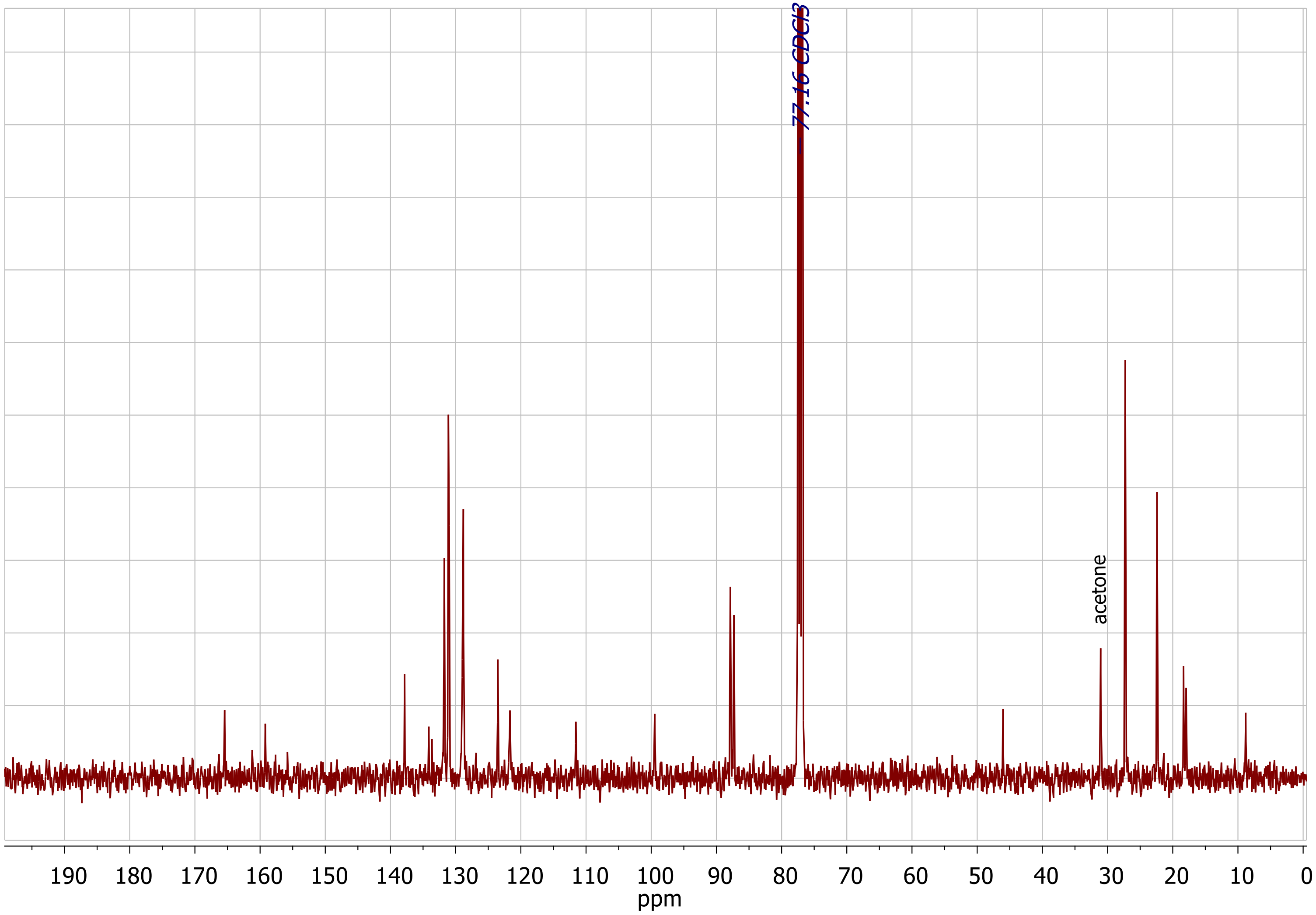


Figure 28S. ^{29}Si{^{1}H} NMR spectrum of [Ru(C_2O_4)(η^6-*p*-cymene){κ*P*-Ph_2PO(2-C_6H_4($SiMe_2{}^tBu$))}], **6**, in $CDCl_3$.

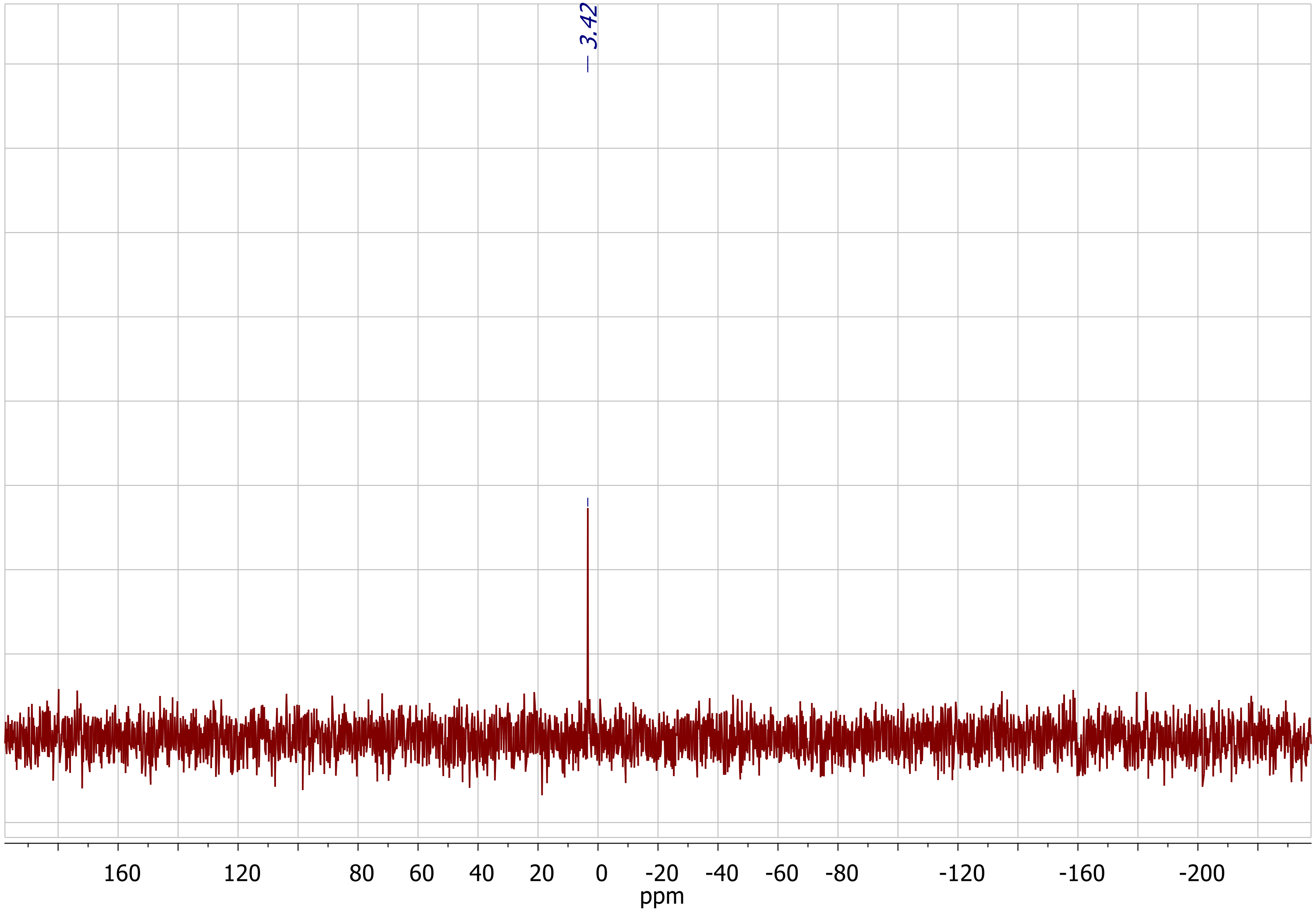


Figure 29S. $^{31}P\{^1H\}$ NMR spectrum of $[Ru(C_2O_4)(\eta^6\text{-}p\text{-cymene})\{\kappa P\text{-}Ph_2PO(2\text{-}C_6H_4(SiMe_2{}^tBu))\}]$, **6**, in $CDCl_3$.

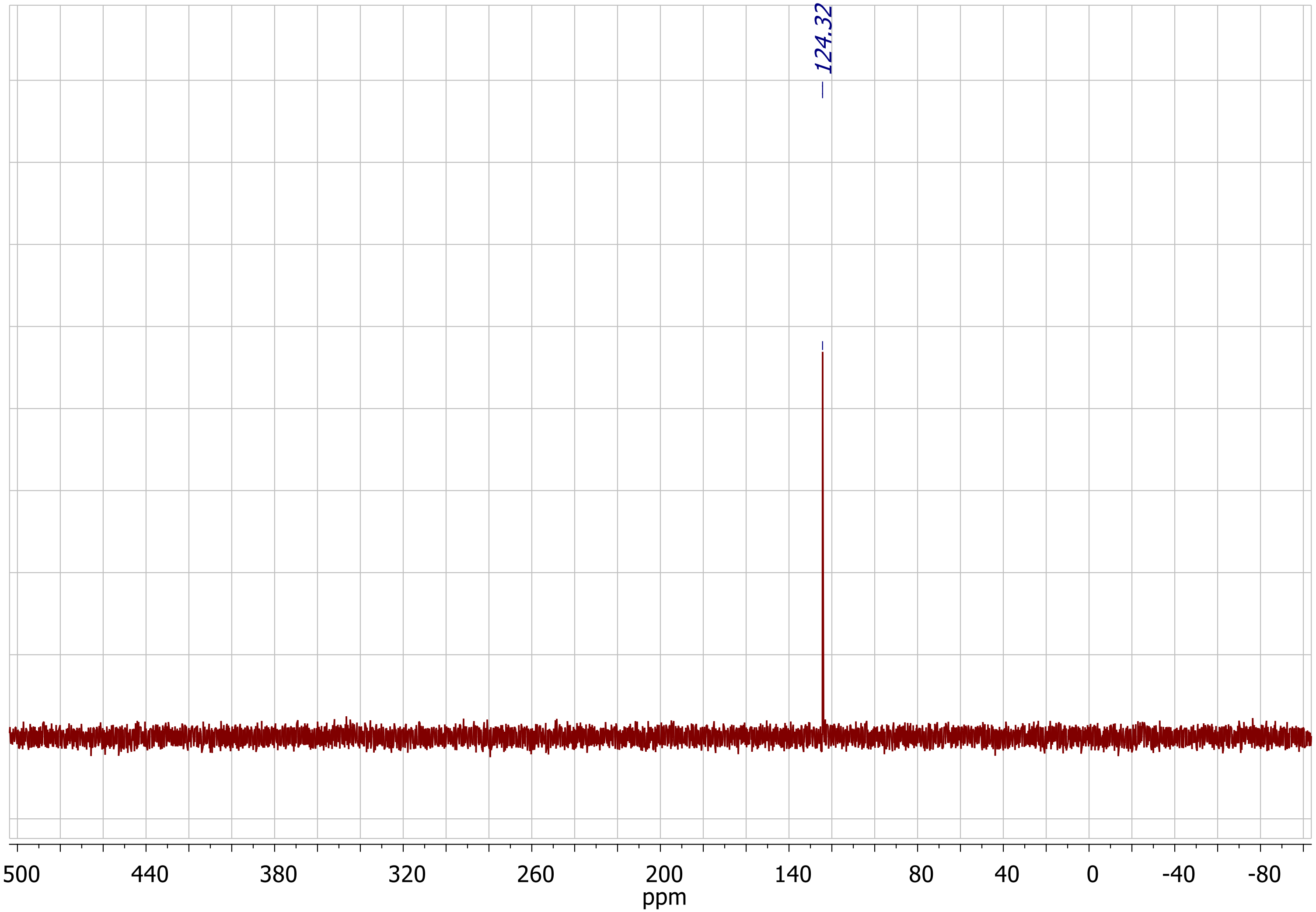


Figure 30S. ^{1}H NMR spectrum of [RuCl$_2$(η^6-*p*-cymene)(κ*P*-PPh$_3$)], **Ru-PPh$_3$**, in CDCl$_3$.

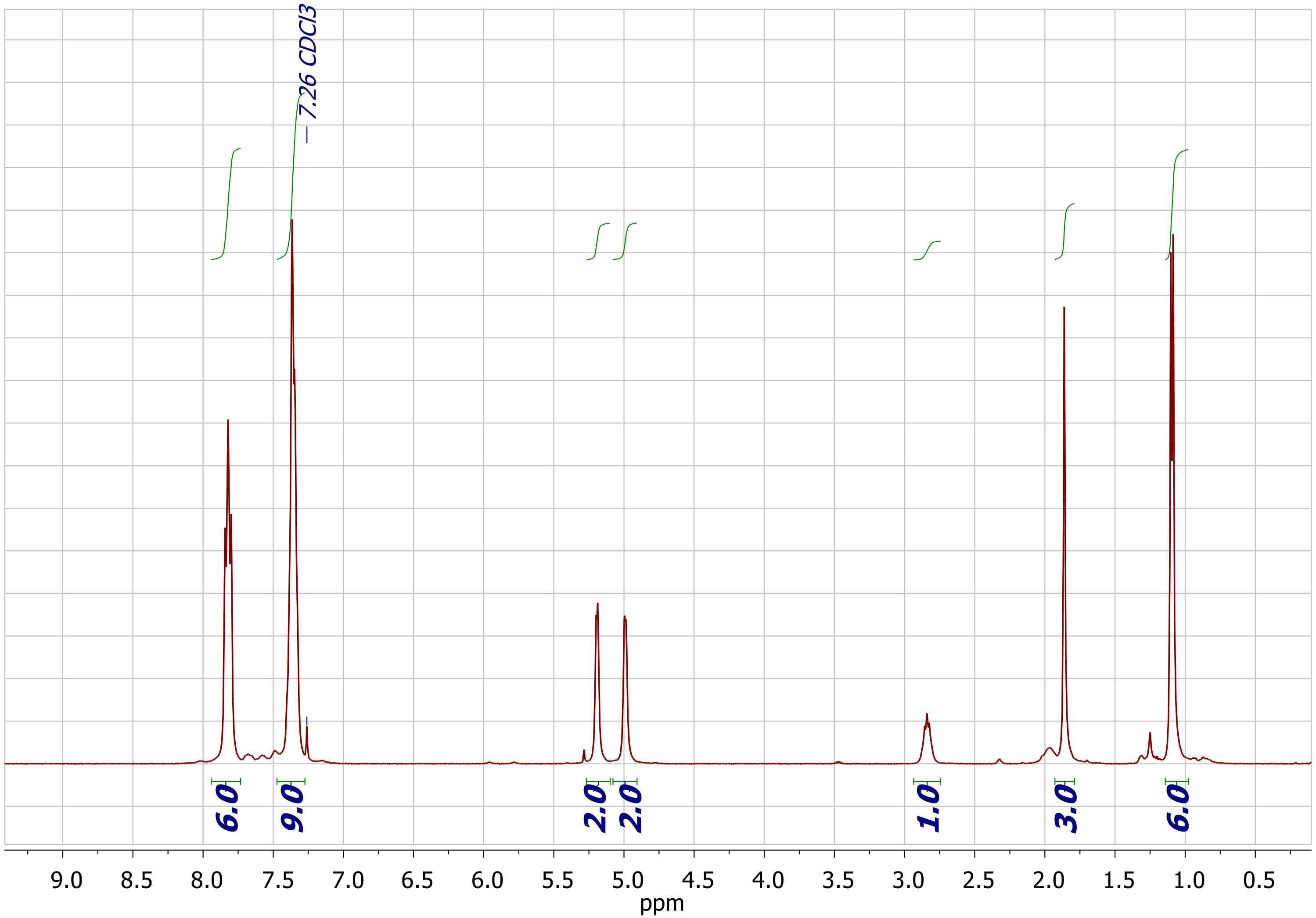


Figure 31S. $^{13}C\{^{1}H\}$ NMR spectrum of [RuCl$_2$(η^6-*p*-cymene)(κ*P*-PPh$_3$)], **Ru-PPh$_3$**, in CDCl$_3$.

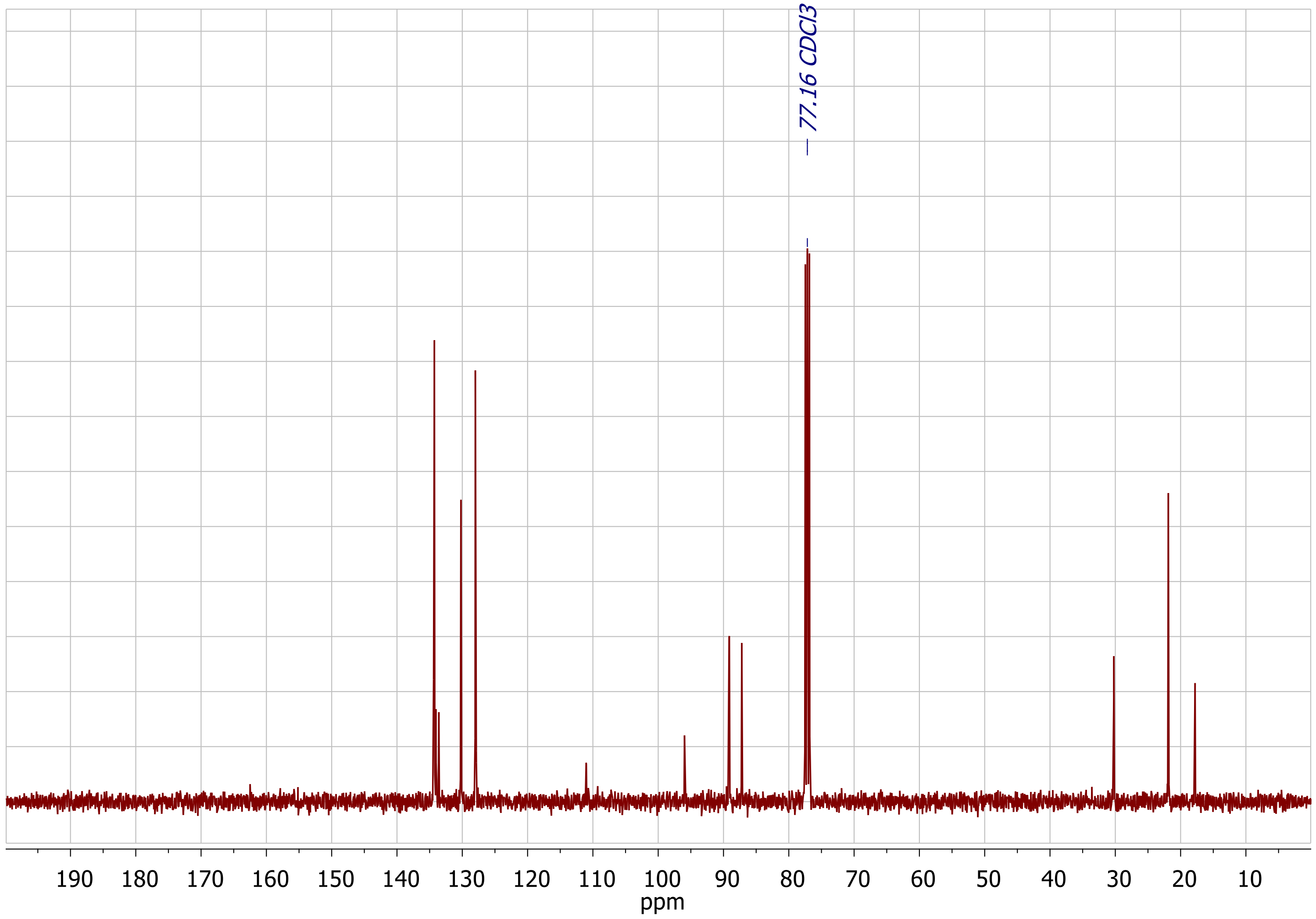


Figure 32S. $^{31}P\{^1H\}$ NMR spectrum of $[RuCl_2(\eta^6\text{-}p\text{-cymene})(\kappa P\text{-}PPh_3)]$, **$Ru\text{-}PPh_3$**, in $CDCl_3$.

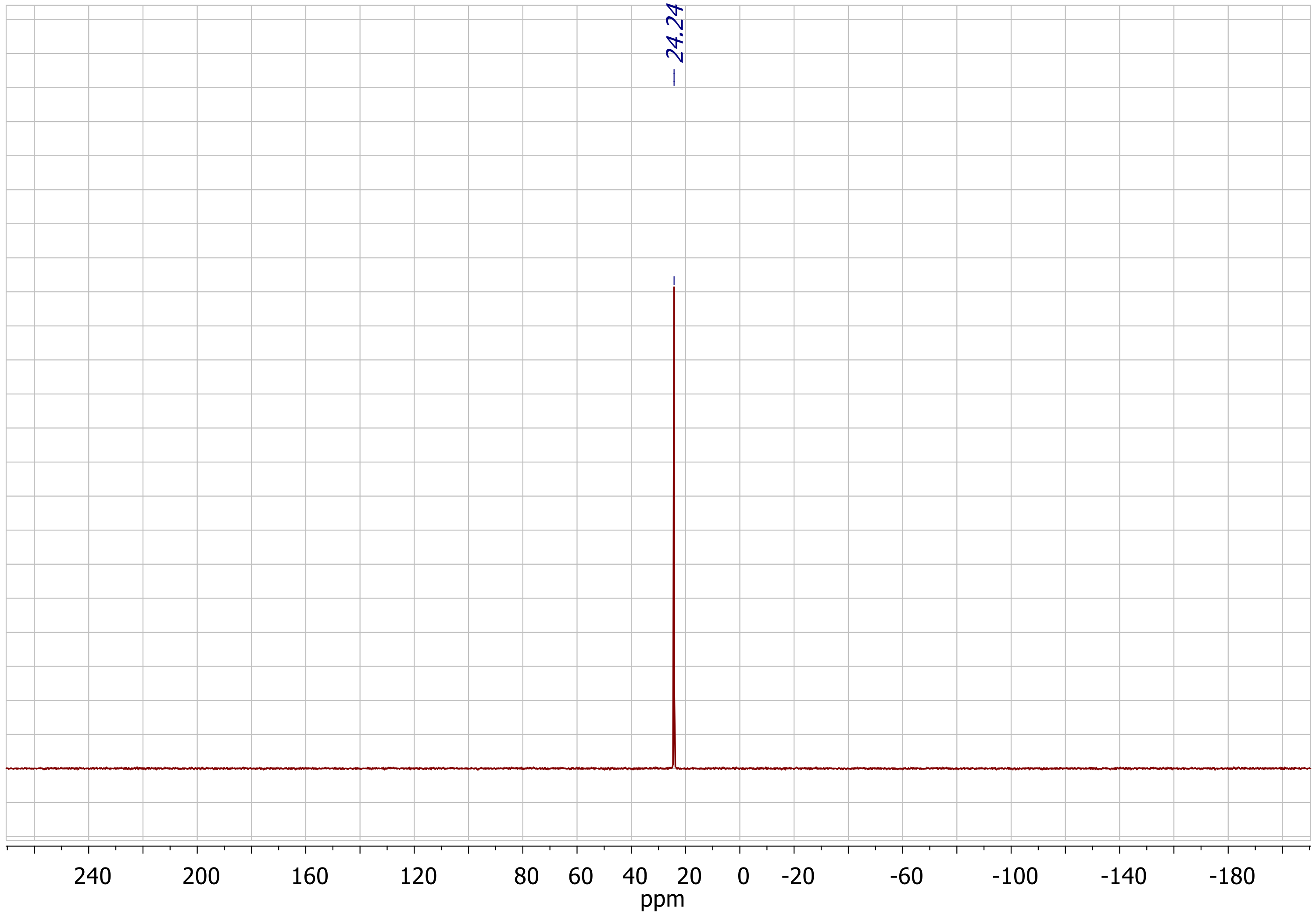


Figure 33S. ^{1}H NMR spectrum of [Ru(C_2O_4)(η^6-*p*-cymene)(κ*P*-PPh_3)], **Ru-PPh$_3$-O** in CD_3OD.

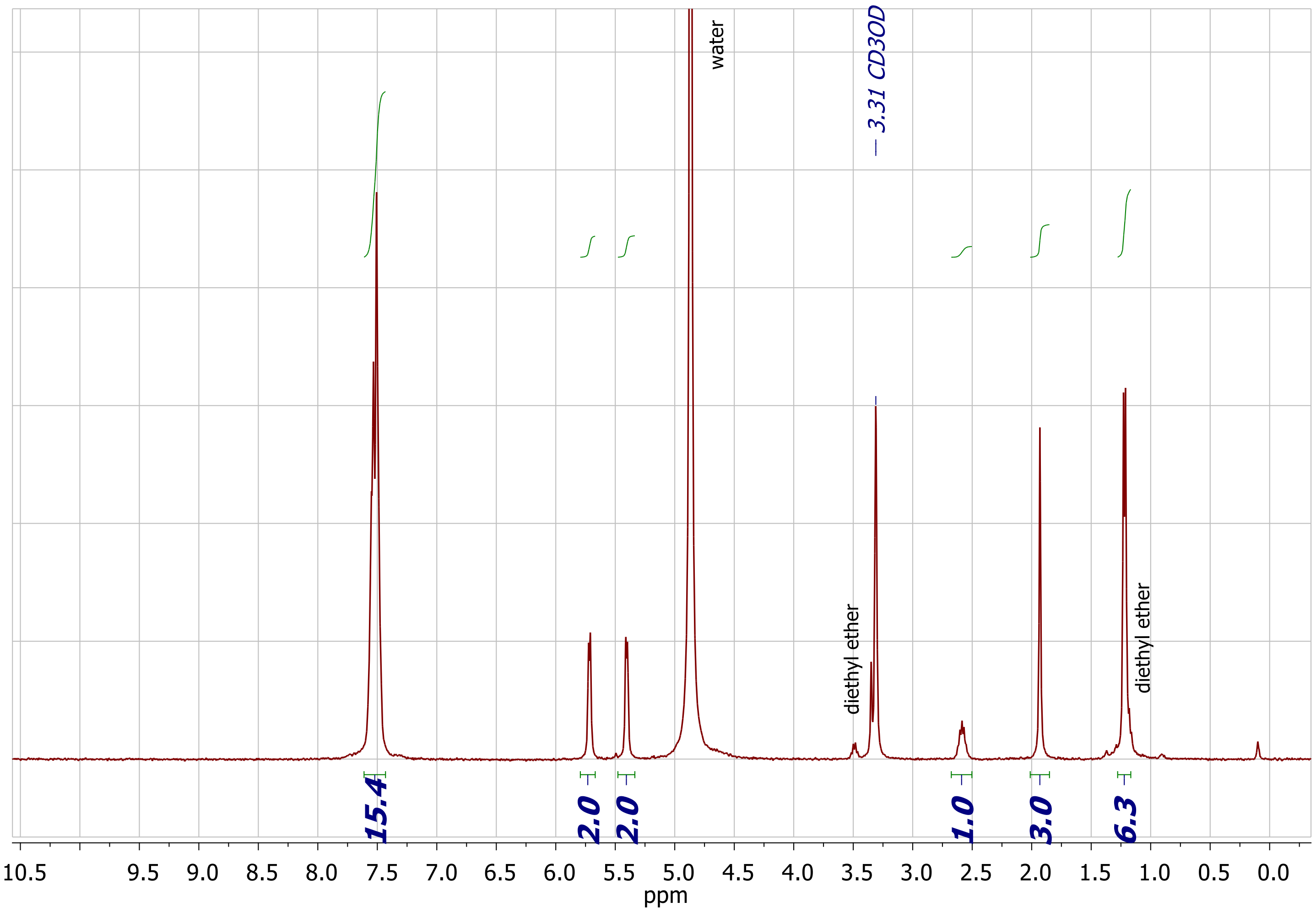


Figure 34S. $^{13}C\{^1H\}$ NMR spectrum of $[Ru(C_2O_4)(\eta^6\text{-}p\text{-cymene})(\kappa P\text{-}PPh_3)]$, **Ru-PPh$_3$-O** in CD_3OD.

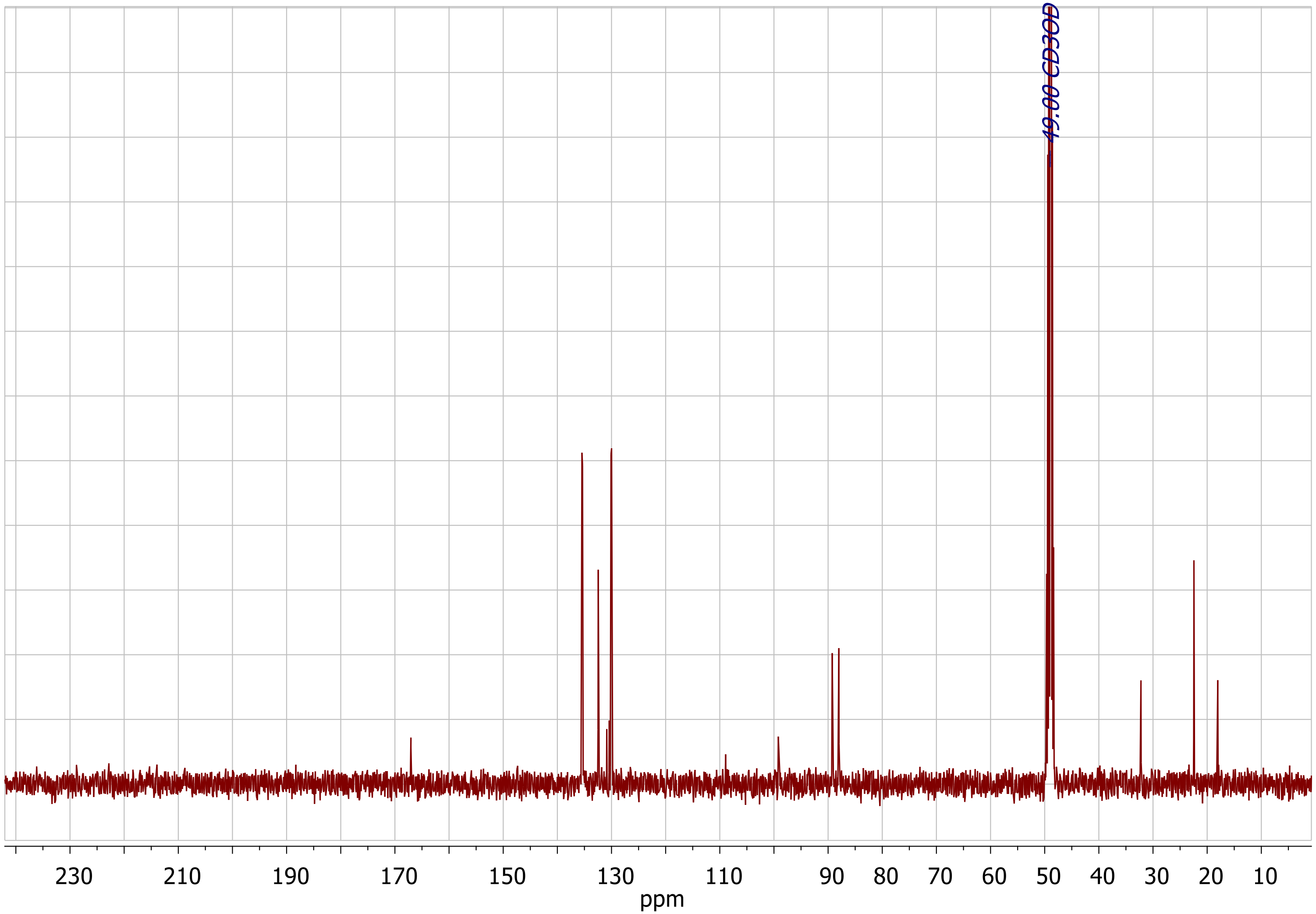
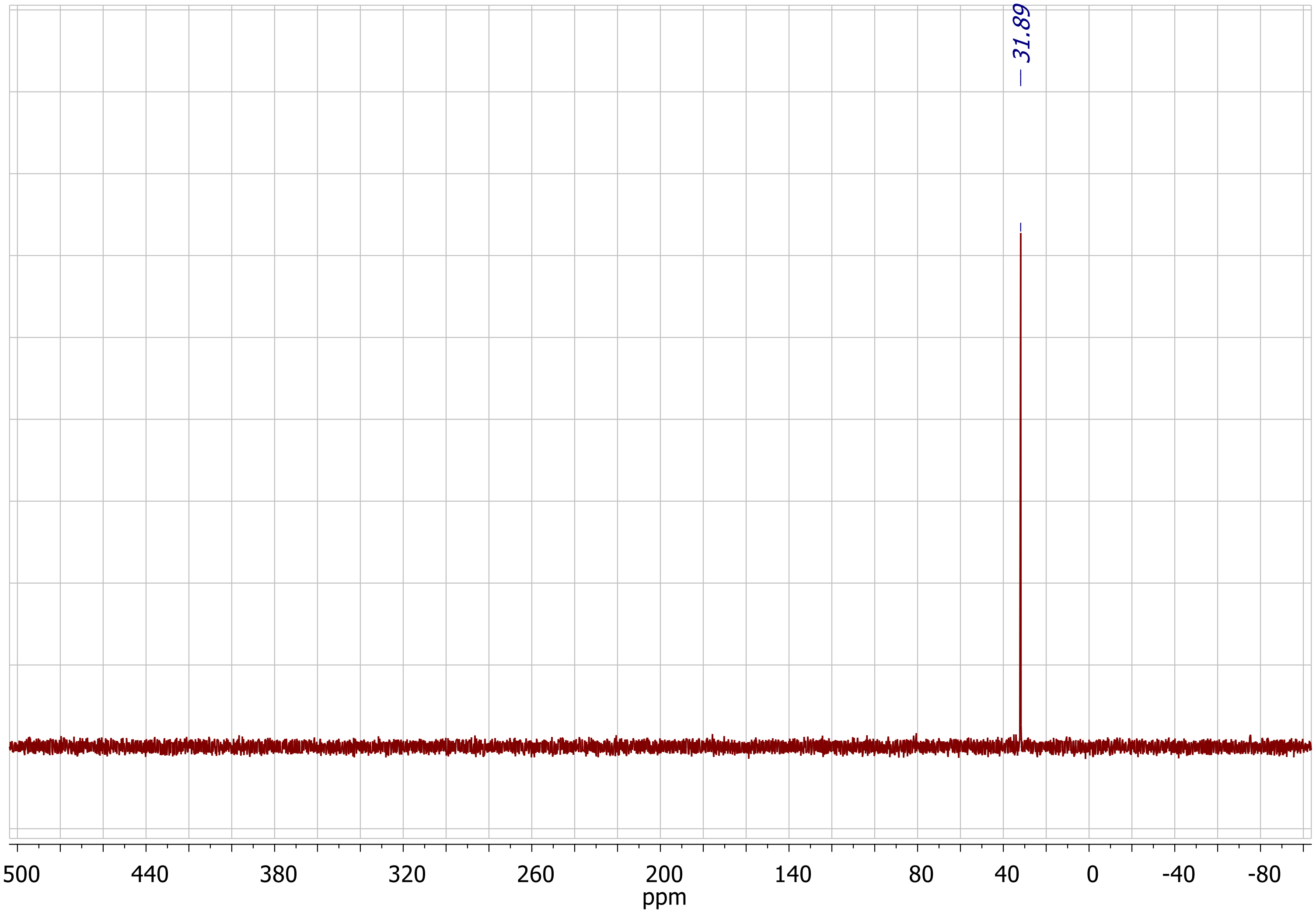


Figure 35S. $^{31}P\{^{1}H\}$ NMR spectrum of $[Ru(C_2O_4)(\eta^6$-*p*-cymene)(κ*P*-$PPh_3)]$, **Ru-PPh$_3$-O** in CD_3OD.



Stability studies in DMSO/water solutions.

Reference data (NMR). NMR spectra of the following compounds were recorded in DMSO-d_6/D_2O 9:1 *v*/*v* and used as reference for NMR assignments.

***p*-cymene**. ^{1}H NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 7.12–7.03 (m, 4H), 2.80 (hept, $^3J_{HH}$ = 6.9 Hz, 1H), 2.23 (s, 3H), 1.15 (d, $^3J_{HH}$ = 6.9 Hz, 6H). ^{13}C{^{1}H} NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 144.6, 133.6, 128.1, 125.3, 32.2, 23.1, 19.7.

$Ph_2P(4\text{-}C_6H_4OSiMe_2{}^tBu)$. Immediate decomposition upon dissolution. ^{31}P{^{1}H} NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 36.2, 34.8, 30.8, 27.2, -7.0, -8.5, -24.3, -25.7.

$^tBuMe_2SiOH$.[12] ^{1}H NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 0.82 (s, 9H), -0.06 (s, 6H). ^{29}Si{^{1}H} NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 14.6.

$Ph_2P(4\text{-}C_6H_4Br)$. ^{1}H NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 7.58 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 7.43–7.38 (m, 6H), 7.25–7.19 (m, 4H), 7.15 (t, $^3J_{HH}$ = $^3J_{HP}$ = 7.6 Hz, 2H). ^{31}P{^{1}H} NMR (DMSO-d_6:D_2O 9:1): δ/ppm = –8.0.

$O{=}Ph_2P(4\text{-}C_6H_4Br)$.[13] ^{1}H NMR (DMSO-$d_6$:$D_2O$ 9:1): δ/ppm = 7.76 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.70–7.50 (m, 12H). ^{31}P{^{1}H} NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 27.0.

Cl_2CHCO_2H. ^{1}H NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 6.61 (s, 1H), 4.23 (s, 1H).

Ph_2POPh. ^{1}H NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 7.60–7.55 (m, 4H), 7.48–7.41 (m, 6H), 7.31 (t, $^3J_{HH}$ = $^3J_{HP}$ = 7.9 Hz, 2H), 7.11 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 7.04 (t, $^3J_{HH}$ = 7.3 Hz, 1H). ^{31}P{^{1}H} NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 109.0. Decomposition into phenol and several P-containing species within 24 hours. ^{1}H NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 9.53 (s, PhOH), 8.69 (s), 7.72 (dd, *J* = 13.5, 7.5 Hz), 7.65–7.53 (m), 7.16 (t, *J* = 7.8 Hz, 2H, PhOH), 6.76 (dd, *J* = 11.0, 7.9 Hz, 3H, PhOH). ^{31}P{^{1}H} NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 29.9, 23.7, 20.4, 20.3, 19.8, 19.3, -24.3, -25.7.

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[12] The compound was prepared according to the literature: P. Patschinski, C. Zhang and H. Zipse, *J. Org. Chem.*, 2014, **79**, 8348-8357.

[13] The same compound was formed upon air exposure of the phosphine in DMSO/D2O solution at ambient temperature for several days.

$Ph_2P(O(2\text{-}C_6H_4SiMe_2{}^tBu))$. Immediate decomposition upon dissolution. $^{31}P\{^1H\}$ NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 106.8, 36.2, 34.8, 29.9, 29.4, 28.5, 24.2, 22.6, 20.4, 19.8, 19.3, -18.1, -24.3, -25.7.

$2\text{-}C_6H_4(OH)(SiMe_2{}^tBu)$. ^1H NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 9.40 (s, 1H), 7.22 (d, $^3J_{HH}$ = 6.8 Hz, 1H), 7.16 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 6.79–6.66 (m, 2H), 0.84 (s, 9H), 0.22 (s, 6H). $^{29}Si\{^1H\}$ NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 7.52.

$[Bu_4N]_2[C_2O_4]$.[14] $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ/ppm = 174.1.

PPh_3. ^1H NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 7.40–7.35 (m, 9H), 7.25–7.18 (m, 6H). $^{31}P\{^1H\}$ NMR (DMSO-d_6:D_2O 9:1): δ/ppm = –7.0.

$O{=}PPh_3$.[13] ^1H NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 7.65–7.51 (m, 15H). $^{31}P\{^1H\}$ NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 27.4.

Reference data (conductivity). **NaCl**. Λ_m (DMSO:H_2O 9:1, c = $1.0\cdot10^{-3}$ M) = 48 $S\cdot cm^2\cdot mol^{-1}$. **$NaNO_3$**. Λ_m (DMSO:H_2O 9:1, c = $1.0\cdot10^{-3}$ M) = 49 $S\cdot cm^2\cdot mol^{-1}$.

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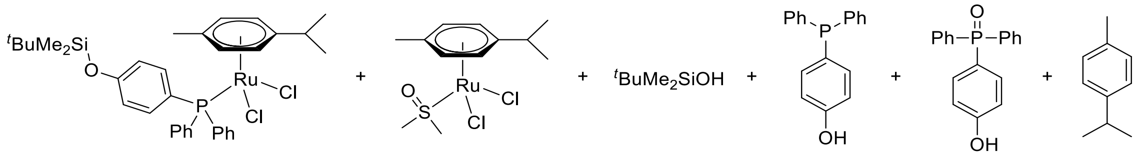
[14] M. Más-Montoya, D. Curiel, C. Ramírez de Arellano, A. Tárraga and P. Molina, *Eur. J. Org. Chem.*, 2016, **22**, 3878-3883.

Stability studies in DMSO/water: *compound **1***. Red-orange solution (Scheme 1S, Table 2S).

1. ^{1}H NMR (DMSO-d$_6$:D$_2$O 9:1): δ/ppm = 7.73–7.66 (m, 4H), 7.60 (t, *J* = 9.2 Hz, 2H), 7.44–7.33 (m, 6H), 6.85 (d, *J* = 7.9 Hz, 2H), 5.27 (d, *J* = 6.0 Hz, 2H), 5.20 (d, *J* = 5.7 Hz, 2H), 1.74 (s, 3H), 1.00–0.85 (m, 15H), 0.18 (s, 6H). ^{31}P{^{1}H} NMR (DMSO-d$_6$:D$_2$O 9:1): δ/ppm = 23.2. **P1**. ^{1}H NMR (DMSO-d$_6$:D$_2$O 9:1): δ/ppm = 7.23–7.12 (m), 6.81 (d, *J* = 7.7 Hz, 2H). ^{31}P{^{1}H} NMR (DMSO-d$_6$:D$_2$O 9:1): δ/ppm = –8.5. **P1=O**. ^{1}H NMR (DMSO-d$_6$:D$_2$O 9:1): δ/ppm = 7.82–7.75 (m), 6.72 (d, *J* = 8.3 Hz, 2H). ^{31}P{^{1}H} NMR (DMSO-d$_6$:D$_2$O 9:1): δ/ppm = 27.5. **Minor P-containing species**. ^{1}H NMR (DMSO-d$_6$:D$_2$O 9:1): δ/ppm = 36.5 (7.5-72 h), 27.2 (72 h), 27.5 (72 h), 23.1 (23.5-72 h).

Scheme 1S and **Table 2S**. Molar conductivity and NMR detected species as a function of time for DMSO/water 9:1 *v*/*v* solution of **1** at 37°C.



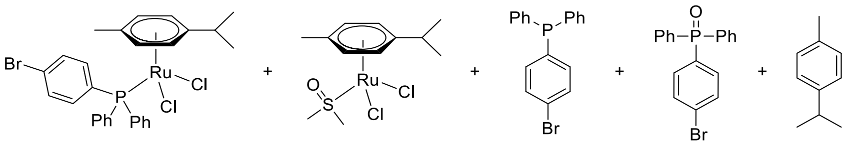
1 **S1** **P1** **O=P1**

time / hours		0	7.5	23.5	48	72
Λ$_m$ / S·cm^2·mol^{-1}		20	24	31	36	44
% NMR	***1** vs. internal standard*	97	90	70	24	9
	1	86	73	51	15	6
	S1	7	7	2	0	0
	^{t}BuMe$_2$SiOH	3	6	12	17	18
	P1	0	2	7	15	18
	O=P1	3	4	5	7	7
	***p*-cymene**	1	8	23	46	51

Stability studies in DMSO/water: *compound **2***. Red-orange solution (Scheme 2S, Table 3S).

2. ^{1}H NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 7.74–7.67 (m, 4H), 7.65 (t, *J* = 9.0 Hz, 2H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.50–7.40 (m, 6H), 5.30 (d, *J* = 6.0 Hz, 2H), 5.23 (d, *J* = 5.8 Hz, 2H), 1.74 (s, 3H), 0.93 (d, *J* = 6.9 Hz, 6H). ^{31}P{^{1}H} NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 24.5. **Minor P-containing species**. ^{31}P{^{1}H} NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 42.7 (72 h), 38.3 (23.5–72 h).

Scheme 2S and **Table 3S**. Molar conductivity and NMR detected species as a function of time for DMSO/water 9:1 *v*/*v* solution of **2** at 37°C.



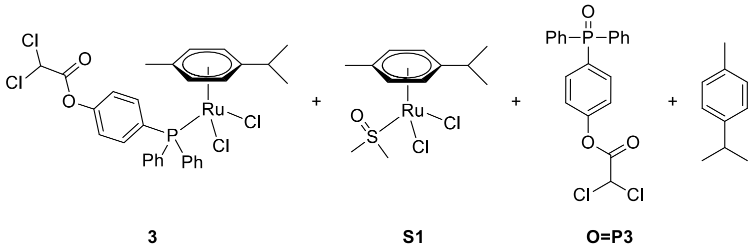
2 **S1** **P2** **O=P2**

time / hours		0	7.5	23.5	48	72
Λ_m / $S\cdot cm^2\cdot mol^{-1}$		23	25	26	26	31
% NMR	***2** vs. internal standard*	97	83	67	45	27
	2	90	82	57	32	17
	S1	4	3	2	0	0
	P2	6	6	9	22	29
	O=P2	0	0	12	13	13
	***p*-cymene**	0	9	20	33	41

Stability studies in DMSO/water: *compound 3*. Red-orange solution (Scheme 3S, Table 4S).

3. ^{1}H NMR (DMSO-d$_6$:D$_2$O 9:1): δ/ppm = 7.72–7.65 (m, 4H), 7.54 (t, *J* = 8.8 Hz, 2H), 7.46–7.32 (m, 6H), 6.77 (d, *J* = 7.6 Hz, 2H), 6.37 (s, 1H), 5.26 (d, *J* = 5.3 Hz, 2H), 5.17 (d, *J* = 4.7 Hz, 2H), 1.73 (s, 3H), 0.94 (d, *J* = 6.5 Hz, 6H). ^{31}P{^{1}H} NMR (DMSO-d$_6$:D$_2$O 9:1): δ/ppm = 23.1. **O=P3**. ^{1}H NMR (DMSO-d$_6$:D$_2$O 9:1): δ/ppm = 7.85–7.76 (m), 6.91 (d, *J* = 7.1 Hz, 2H), {6.37 (s)}. ^{31}P{^{1}H} NMR (DMSO-d$_6$:D$_2$O 9:1): δ/ppm = 27.5. **Minor P-containing species**. ^{1}H NMR (DMSO-d$_6$:D$_2$O 9:1): δ/ppm = 7.65–7.56 (m), 7.24–7.15 (m). ^{31}P{^{1}H} NMR (DMSO-d$_6$:D$_2$O 9:1): δ/ppm = 36.6 (23.5-72 h), 40.1 (48-72 h).

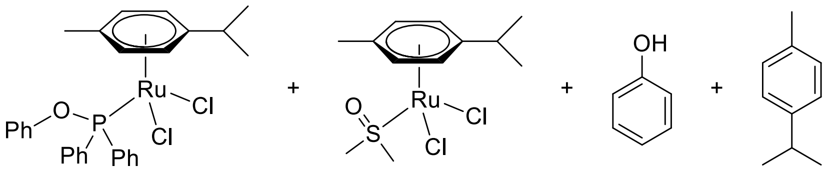
Scheme 3S and **Table 4S**. Molar conductivity and NMR detected species as a function of time for DMSO/water 9:1 *v*/*v* solution of **3** at 37°C.



time / hours		0	7.5	23.5	48	72
Λ$_m$ / S·cm^2·mol^{-1}		20	24	31	36	44
% NMR	***3** vs. internal standard*	95	89	56	37	15
	3	83	74	54	30	12
	S1	7	5	2	0	0
	O=P3	10	14	16	17	20
	***p*-cymene**	0	8	28	53	67

Stability studies in DMSO/water: *compound **4***. At variance to the general procedure, a saturated solution in DMSO-d_6/D_2O 9:1 *v*/*v* (orange solution + orange precipitate) was used for the NMR experiment; the solubility of **4** in this solvent being < $1.5 \cdot 10^{-2}$ mol·L^{-1}. A $1.5 \cdot 10^{-3}$ mol·L^{-1} solution of **4** in DMSO/H_2O 9:1 *v*/*v* was used for conductivity measurements. Data are compiled in Table 5S while NMR detected species are shown in Scheme 4S. **4**. ^1H NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 7.90 (t, *J* = 8.4 Hz, 4H), 7.43–7.33 (m, 6H), 7.30–7.21 (m, 4H), 7.07 (t, *J* = 6.1 Hz, 1H), 5.42 (s-br, 4H), 2.29–2.20 (hept, *J* = 6.7 Hz, 1H), 1.30 (s, 3H), 0.70 (d, *J* = 6.5 Hz, 6H). $^{31}P\{^1H\}$ NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 114.6. **Minor P-containing species**. ^1H NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 8.37–8.29 (m), 8.20–8.14 (m), 7.72 (dd, *J* = 12.4, 7.4 Hz), 7.65–7.44 (m), 7.02–6.92 (m), 6.84–6.81 (m). $^{31}P\{^1H\}$ NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 165.0 (48-72 h), 142.3 (23.5-72 h), 142.2 (23.5-72 h), 29.9 (48-72 h), 24.3 (48-72 h).

Scheme 4S and **Table 5S**. Molar conductivity and NMR detected species as a function of time for DMSO/water 9:1 *v*/*v* solution of **4** at 37°C.

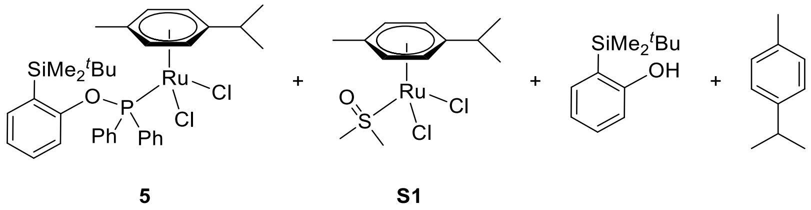


4 **S1**

time / hours		0	7.5	23.5	48	72
Λ_m / S·cm^2·mol^{-1}		20	24	31	36	44
% NMR	***4** vs. internal standard*	94	78	25	14	12
	4	95	68	32	14	11
	S1	0	3	9	10	11
	PhOH	5	16	29	35	35
	***p*-cymene**	0	13	30	41	43

Stability studies in DMSO/water: *compound* **5.** At variance to the general procedure, a saturated solution in DMSO-d_6/D_2O 9:1 *v*/*v* (orange solution + orange precipitate) was used for the NMR experiment, the solubility of **5** in this solvent being < $1.5 \cdot 10^{-2}$ mol·L^{-1}. A $1.5 \cdot 10^{-3}$ mol·L^{-1} solution of **5** in DMSO/H_2O 9:1 *v*/*v* was used for conductivity measurements. Data are compiled in Table 6S while NMR detected species are shown in Scheme 5S. **5.** ^{1}H NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 7.82–7.73 (m, 4H), 7.56–7.31 (m, 8H), 7.16–7.07 (m, 2H), 5.54 (d, *J* = 5.1 Hz, 2H), 5.41 (d, *J* = 4.4 Hz, 2H), 2.38–2.29 (m, 1H), 1.60 (s, 3H), 1.01 (s, 9H), 0.86 (d, *J* = 6.2 Hz, 6H), 0.33 (s, 6H). ^{31}P{^{1}H} NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 122.1. **Other P-containing products**. ^{1}H NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 8.35 (t), 8.30 (d), 7.80-7.30 (m), 0.80 (s), 0.73 (s), 0.59 (s), 0.36 (s), 0.12 (s). ^{31}P{^{1}H} NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 169.6 (72 h), 111.2 (72h), 29.2 (7–72h), 24.3 (22–72 h), 19.7 (22–72 h), 19.2 (22–72 h), 18.8 (22–72 h).

Scheme 5S and **Table 6S**. Molar conductivity and NMR detected species as a function of time for DMSO/water 9:1 *v*/*v* solution of **5** at 37°C.

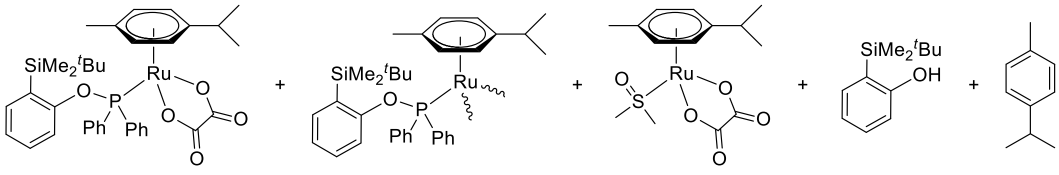


time / hours		0	7	22	48	72
Λ_m / S·cm^2·mol^{-1}		3	14	17	22	24
% NMR	***5** vs. internal standard*	96	48	33	6	4
	5	91	47	18	3	1
	S1	9	24	33	33	28
	2-$C_6H_4(OH)(SiMe_2{}^tBu)$	0	19	32	41	42
	***p*-cymene**	0	10	17	23	29

Stability studies in DMSO/water: *compound **6***. Yellow solution (Scheme 6S and Table 7S).

6. ^{1}H NMR (DMSO-d$_6$:D$_2$O 9:1): δ/ppm = 7.60 (d, *J* = 7.0 Hz, 1H), 7.50–7.45 (m, 3H), 7.44–7.35 (m, 8H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 8.3 Hz, 1H), 5.53 (d, *J* = 5.9 Hz, 2H), 5.29 (d, *J* = 5.9 Hz, 2H), 2.29 (hept, *J* = 6.8 Hz, 1H), 1.73 (s, 3H), 1.11 (d, *J* = 6.8 Hz, 6H), 0.96 (s, 9H), 0.30 (s, 6H). ^{31}P{^{1}H} NMR (DMSO-d$_6$:D$_2$O 9:1): δ/ppm = 127.9. **6a**. ^{1}H NMR (DMSO-d$_6$:D$_2$O 9:1) δ 7.82–7.76 (m, 4H), 5.57 (d, *J* = 3.3 Hz, 2H), 5.39 (d, *J* = 6.1 Hz, 2H), 1.59 (s, 3H), 1.00 (s, 9H), 0.86 (d, 6H), 0.31 (s, 9H). ^{31}P{^{1}H} NMR (DMSO-d$_6$:D$_2$O 9:1): δ/ppm = 122.1 (7.5h-72 h). **Other products**. ^{1}H NMR (DMSO-d$_6$:D$_2$O 9:1) δ 8.31 (m), 6.97, 6.13 (d), 3.15 (s), 2.10 (s), 1.96 (s), 1.91 (s), 1.79 (s), 0.77 (s), 0.72 (s), 0.68 (m), 0.48 (s), 0.27 (m), 0.11 (s). ^{31}P{^{1}H} NMR (DMSO-d$_6$:D$_2$O 9:1): δ/ppm = 174.1 (48–72 h), 106.9 (7.5–23 h), 29.4 (7–72 h), 20.4 (48–72 h), 20.2 (48–72 h), 19.8 (48–72 h), 19.3 (48–72 h).

Scheme 6S and **Table 7S**. Molar conductivity and NMR detected species as a function of time for DMSO/water 9:1 *v*/*v* solution of **6** at 37°C.

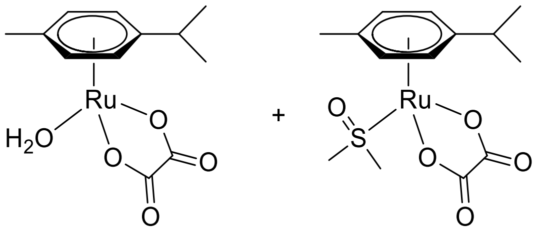


6 **6a** **S2**

time / hours		0	7.5	23	48	72
Λ_m / S·cm^2·mol^{-1}		34	32	33	30	34
% NMR	***6*** *vs. internal standard*	100	84	75	56	33
	6	100	88	75	52	29
	6a	0	4	7	7	5
	S2	0	3	3	4	7
	***o*-C$_6$H$_4$(OH)(SiMe$_2$^{t}Bu)**	0	1	4	15	25
	***p*-cymene**	0	3	9	18	27

Stability studies in DMSO/water: *[Ru(C_2O_4)(η^6-p-cymene)(H_2O)].* Yellow solution (Scheme 7S). [Ru(C_2O_4)(η^6-p-cymene)(Me_2SO)], **S2**. ^{1}H NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 5.96 (s-br, 2H), 5.86 (s-br, 2H), 2.83–2.68 (m, 1H), 2.13 (s, 3H), 1.24 (d, *J* = 6.0 Hz, 6H). ^{13}C{^{1}H} NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 164.9, 105.7, 100.2, 86.8, 86.1, 30.8, 22.4, 17.6. [Ru(C_2O_4)(η^6-p-cymene)(H_2O)]. ^{1}H NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 5.72 (s-br, 2H), 5.48 (s-br, 2H), {2.83–2.68 (m)}, {2.13 (s)}, {1.24 (d)}. ^{13}C{^{1}H} NMR (DMSO-d_6:D_2O 9:1): δ/ppm = 165.7, 98.1, 96.0, 80.4, 77.5, 31.0, 22.5, {17.6}. [Ru(C_2O_4)(η^6-p-cymene)(H_2O)]/**S2** ratio = ca. 0.61. ^{1}H spectrum after 24 hours at 37°C showed partial release of *p*-cymene (*ca.* 13%) but no variation in the compounds ratio, suggesting that equilibrium had been reached.

Scheme 7S. NMR detected species for DMSO/water 9:1 *v*/*v* solution of [Ru(C_2O_4)(η^6-*p*-cymene)(H_2O)].

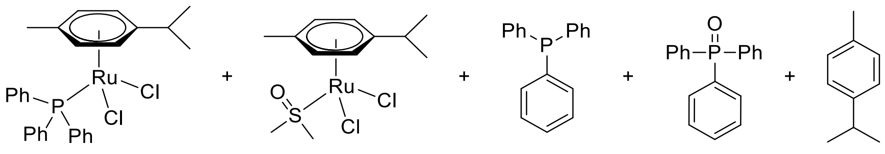


S2

Stability studies in DMSO/water: *[RuCl$_2$(η^6-p-cymene)(κP-PPh$_3$)]* ***(Ru-PPh$_3$)***. Orange solution (Scheme 8S and Table 8S). **Ru-PPh$_3$**. ^{1}H NMR (DMSO-d$_6$:D$_2$O 9:1): δ/ppm = 7.77–7.66 (m, 6H), 7.46–7.35 (m, 9H), 5.27 (d, *J* = 5.9 Hz, 2H), 5.21 (d, *J* = 5.6 Hz, 2H), 1.74 (s, 3H), 0.93 (d, *J* = 6.8 Hz, 6H). ^{31}P{^{1}H} NMR (DMSO-d$_6$:D$_2$O 9:1): δ/ppm = 24.2. **Minor P-containing species**. ^{31}P{^{1}H} NMR (DMSO-d$_6$:D$_2$O 9:1): δ/ppm = 38.1 (72 h).

^{35}Cl NMR (DMSO-d$_6$:D$_2$O 9:1, 72 h): δ/ppm = no signal was observed after 1 hour acquisition time.

Scheme 8S and **Table 8S**. Molar conductivity and NMR detected species as a function of time for DMSO/water 9:1 *v*/*v* solution of **Ru-PPh$_3$** at 37°C.

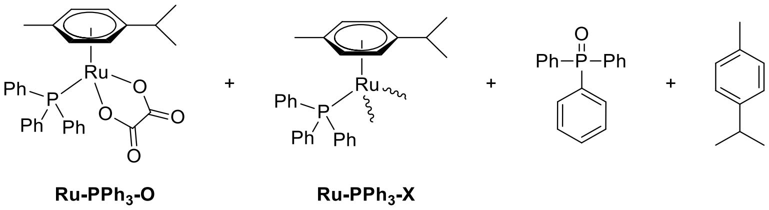


Ru-PPh$_3$ **S1**

time / hours		0	7.5	23.5	48	72
Λ_m / S·cm^2·mol^{-1}		28	27	31	33	34
% NMR	***Ru-PPh$_3$*** *vs. internal standard*	98	90	77	56	30
	Ru-PPh$_3$	91	76	54	34	17
	S1	4	3	1	0	0
	PPh$_3$	4	7	16	28	34
	O=PPh$_3$	1	1	4	4	6
	***p*-cymene**	0	13	25	34	43

Stability studies in DMSO/water: *[Ru(C_2O_4)(η^6-p-cymene)(κP-PPh_3)]* ***(Ru-PPh$_3$-O)***. Yellow-green solution (Scheme 9S and Table 9S). **Ru-PPh$_3$-O**. ^{1}H NMR (DMSO-d$_6$:D_2O 9:1): δ/ppm = 7.56–7.50 (m, 3H), 7.50–7.45 (m, 6H), 7.41–7.36 (m, 6H), 5.67 (d, *J* = 5.9 Hz, 2H), 5.33 (d, *J* = 5.9 Hz, 2H), 2.50–2.43 (m, 1H), 1.77 (s, 3H), 1.10 (d, *J* = 6.8 Hz, 6H). ^{13}C{^{1}H} NMR (DMSO-d$_6$:D_2O 9:1): δ/ppm = 163.3, 133.0 (d, *J* = 10.2 Hz), 130.2 (s), 128.7 (d, *J* = 44.7 Hz), 128.0 (d, *J* = 10.0 Hz), 106.7 (d, *J* = 3.4 Hz), 96.7, 86.9 (d, *J* = 3.7 Hz), 85.5 (d, *J* = 1.7 Hz), 29.5, 20.9, 16.4. ^{31}P{^{1}H} NMR (DMSO-d$_6$:D_2O 9:1): δ/ppm = 32.4. **Ru-PPh$_3$-X**. ^{1}H NMR (DMSO-d$_6$:D_2O 9:1): δ/ppm = 7.74–7.69 (m, 6H), 5.27 (d, *J* = 6.3 Hz, 2H), 5.21 (d, *J* = 5.7 Hz, 2H), 1.74 (s, 3H), 0.93 (d, *J* = 6.8 Hz, 6H). ^{31}P{^{1}H} NMR (DMSO-d$_6$:D_2O 9:1): δ/ppm = 24.2. **Minor P-containing species** (72 h). ^{1}H NMR (DMSO-d$_6$:D_2O 9:1): δ/ppm = 7.75–7.57 (m), 7.27–7.22 (m). ^{31}P{^{1}H} NMR (DMSO-d$_6$:D_2O 9:1): δ/ppm = 45.3, 40.4, 40.1, 27.4 (**O=PPh$_3$**).

Scheme 9S and **Table 9S**. Molar conductivity and NMR detected species as a function of time for DMSO/water 9:1 *v/v* solution of **Ru-PPh$_3$-O** at 37°C.

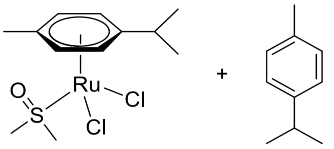


time / hours		0	7.5	23	48	72
Λ_m / S·cm^2·mol^{-1}		24	24	21	23	24
% NMR	**Ru-PPh$_3$-O** *vs. internal standard*	99	84	77	74	64
	Ru-PPh$_3$-O	99	91	86	79	72
	Ru-PPh$_3$-X	0	3	4	4	4
	O=PPh$_3$ + other P species	1	4	5	5	5
	***p*-cymene**	0	2	5	12	19

Stability studies in DMSO/water: *[RuCl$_2$(η^6-p-cymene)]$_2$*. Orange solution (Scheme 10S and Table 10S). **S1**. ^{1}H NMR (DMSO-d$_6$:D$_2$O 9:1): δ/ppm = 5.79 (d, $^3J_{HH}$ = 6.3 Hz, 2H), 5.74 (d, $^3J_{HH}$ = 6.3 Hz, 2H), 2.79 (hept, $^3J_{HH}$ = 6.9 Hz, 1H), 2.07 (s, 3H), 1.17 (d, $^3J_{HH}$ = 6.9 Hz, 6H). ^{13}C{^{1}H} NMR (DMSO-d$_6$:D$_2$O 9:1): δ/ppm = 107.2, 100.7, 86.8, 85.9, 30.5, 21.9, 18.3. ^{35}Cl NMR (DMSO-d$_6$:D$_2$O 9:1): δ/ppm = no signal.

^{1}H NMR spectra in DMSO-d$_6$ and DMSO-d$_6$/D$_2$O 9:1 *v*/*v* + NaCl (0.11 mol·L^{-1}) showed a single set of signals identical to that in DMSO-d$_6$/D$_2$O 9:1 *v*/*v* (vide infra), due to the formation of [(η^6-*p*-cymene)RuCl$_2$(κ*S*-Me$_2$SO)] (**S1**).[15]

Scheme 10S and **Table 10S**. Molar conductivity and NMR detected species as a function of time for DMSO/water 9:1 *v*/*v* solution of [RuCl$_2$(η^6-*p*-cymene)]$_2$ at 37°C.



S1

time / hours		0 - 7.5	24 - 48	72
Λ_m / S·cm^2·mol^{-1}		7.0		
% NMR	**S1**	100	98	96
	***p*-cymene**	0	2	4

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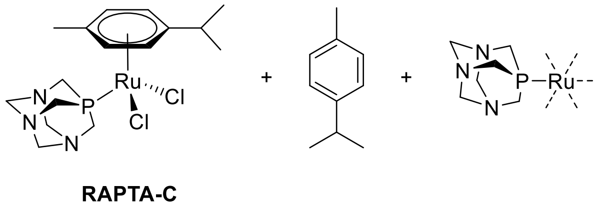
[15] M. Patra, T. Joshi, V. Pierroz, K. Ingram, M. Kaiser, S. Ferrari, B. Spingler, J. Keiser and G. Gasser, *Chem. Eur. J.*, 2013, **19**, 14768–14772.

Stability studies in DMSO/water: *[RuCl$_2$(η^6-p-cymene)(PTA)]* ***(RAPTA-C)***. Orange solution (Scheme 11S and Table 11S). **RAPTA-C**. ^{1}H NMR (DMSO-d$_6$:D$_2$O 9:1): δ/ppm = 5.72 (d, $^3J_{HH}$ = 5.7 Hz, 2H), 5.69 (d, $^3J_{HH}$ = 5.7 Hz, 2H), 4.41 (s, 6H), 4.14 (s, 6H), 1.86 (s, 3H), 1.09 (d, $^3J_{HH}$ = 6.8 Hz, 6H). ^{31}P{^{1}H} NMR: δ/ppm = -34.1. **Other Ru-pta species**. ^{1}H NMR (DMSO-d$_6$:D$_2$O 9:1): δ/ppm = 4.37 (s, 6H), 4.16 (s, 6H). ^{31}P{^{1}H} NMR: δ/ppm = -19.9.

Scheme 11S and **Table 11S**. Molar conductivity and NMR detected species as a function of time for DMSO/water 9:1 *v*/*v* solution of [RuCl$_2$(η^6-*p*-cymene)(PTA)] at 37°C.



time / hours		0	16.5	40.5	72
Λ_m / S·cm^2·mol^{-1}		24			
% NMR	**RAPTA-C** *vs. internal standard*	100	90	63	52
	RAPTA-C	100	57	38	28
	***p*-cymene**	0	24	31	37
	Other Ru-pta	0	19	31	35

Stability studies in chloroform solutions.

General procedure. Ruthenium compounds (ca. 0.3 mmol) were dissolved in $CDCl_3$ and the resulting solutions were stored at ambient temperature and analysed by $^{1}H/^{31}P$ NMR spectroscopy.

[RuCl$_2$(η^6-*p*-cymene){κ*P*-Ph$_2$P(4-C$_6$H$_4$OSiMe$_2$^{t}Bu)}], 5. Orange solution. After 14 days, ^{1}H NMR spectrum indicated extensive degradation with release of *p*-cymene.

[Ru(C$_2$O$_4$)(η^6-*p*-cymene){κ*P*-Ph$_2$P(O(2-C$_6$H$_4$SiMe$_2$^{t}Bu))}], 6. Yellow solution. After 12 days, ^{1}H NMR spectrum indicated extensive degradation with release of *p*-cymene. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ/ppm = 120.3, 30.0.

[RuCl$_2$(η^6-*p*-cymene)(κ*P*-PPh$_3$)], Ru-PPh$_3$. Orange red-solution developing a brown-green colour within weeks followed by the precipitation of a dark solid. ^{1}H and ^{31}P NMR spectra of the solution indicated a partial degradation of the starting material with release of *p*-cymene. After 2 months, volatiles were removed under vacuum affording a dark brown solid. Brown crystals were obtained from a MeOH/acetone (1:1 *v*/*v*) solution of the solid layered with Et_2O and settled aside at -20°C. The Ru(II)/Ru(III) mixed valence compound [(η^6-*p*-cymene)Ru(μ-Cl)$_3$RuCl$_2$(PPh$_3$)] (**7**)[16] was identified by X-Ray analysis.

[Ru(C$_2$O$_4$)(η^6-*p*-cymene)(κ*P*-PPh$_3$)], Ru-PPh$_3$-O. Yellow solution turning into an orange solution with precipitate within hours. ^{1}H NMR spectrum indicated almost complete conversion to another species containing the {Ru(*p*-cymene)(PPh$_3$)} fragment. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.86–7.80 (m, 6H), 7.41–7.33 (m, 9H), 5.19 (d, J = 6.0 Hz, 2H), 4.99 (d, J = 5.6 Hz, 2H), 2.85 (hept, J = 6.8 Hz, 1H), 1.87 (s, 3H), 1.10 (d, J = 6.9 Hz, 6H). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ/ppm = 24.2.

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[16] J. Wolf, K. Thommes, O. Briel, R. Scopelliti and K. Severin, *Organometallics*, 2008, **27**, 4464-4474.

Table 12S. Selected bond distances (Å) and angles (°) for **3**.

Ru(1)−(η^6-p-cymene)$_{av}$	2.21(3)	Ru(1)−P(1)	2.347(3)
Ru(1)−Cl(1)	2.401(3)	Ru(1)−Cl(2)	2.406(4)
P(1)−C(11)	1.832(13)	P(1)−C(17)	1.833(13)
P(1)−C(23)	1.830(13)	C(26)−O(1)	1.376(18)
C(29)−O(1)	1.28(2)	C(29)−O(2)	1.22(2)
C(29)−C(30)	1.54(3)	C(30)−Cl(3)	1.78(2)
C(30)−Cl(4)	1.72(2)		
Cl(1)−Ru(1)−Cl(2)	87.29(13)	Cl(1)−Ru(1)−P(1)	89.03(11)
Cl(2)−Ru(1)−P(1)	85.82(12)	C(26)−O(1)−C(29)	120.9(14)
O(1)−C(29)−O(2)	125.7(19)	O(1)−C(29)−C(30)	112.6(16)
O(2)−C(29)−C(30)	121.7(18)		

Table 13S. Selected bond distances (Å) and angles (°) for **4**.

Ru(1)−(η^6-p-cymene)$_{av}$	2.22(2)	Ru(1)−P(1)	2.316(2)
Ru(1)−Cl(1)	2.406(3)	Ru(1)−Cl(2)	2.417(2)
P(1)−C(17)	1.812(9)	P(1)−C(23)	1.837(9)
P(1)−O(1)	1.627(6)	O(1)−C(11)	1.399(10)
Cl(1)−Ru(1)−Cl(2)	88.51(9)	Cl(1)−Ru(1)−P(1)	92.54(8)
Cl(2)−Ru(1)−P(1)	85.83(8)	P(1)−O(1)−C(11)	125.7(6)

Table 14S. Selected bond distances (Å) and angles (°) for **5**.

Ru(1)−(η^6-p-cymene)$_{av}$	2.224(10)	Ru(1)−P(1)	2.3154(9)
Ru(1)−Cl(1)	2.4040(9)	Ru(1)−Cl(2)	2.4206(10)
P(1)−C(23)	1.824(4)	P(1)−C(29)	1.831(4)
P(1)−O(1)	1.650(2)	O(1)−C(11)	1.399(4)
C(12)−Si(1)	1.889(4)	C(17)−Si(1)	1.853(4)
C(18)−Si(1)	1.872(4)	C(19)−Si(1)	1.894(4)
Cl(1)−Ru(1)−Cl(2)	86.02(4)	Cl(1)−Ru(1)−P(1)	91.60(3)
Cl(2)−Ru(1)−P(1)	89.23(3)	P(1)−O(1)−C(11)	124.2(2)
C(12)−Si(1)−C(19)	108.28(18)	C(17)−Si(1)−C(18)	108.7(2)

Table 15S. Selected bond distances (Å) and angles (°) for **6**.

Ru(1)−(η^6-p-cymene)$_{av}$	2.223(10)	Ru(1)−P(1)	2.3190(11)
Ru(1)−O(1)	2.079(3)	Ru(1)−O(2)	2.069(3)
C(21)−O(1)	1.289(5)	C(22)−O(2)	1.295(5)
C(21)−O(3)	1.221(5)	C(22)−O(4)	1.214(5)
C(21)−C(22)	1.547(6)	P(1)−O(5)	1.641(2)
P(1)−C(31)	1.827(4)	P(1)−C(37)	1.813(4)
O(5)−C(43)	1.400(4)	C(44)−Si(1)	1.894(4)
C(49)−Si(1)	1.862(4)	C(50)−Si(1)	1.874(4)
C(51)−Si(1)	1.895(4)		
O(1)−Ru(1)−O(2)	78.40(11)	O(1)−Ru(1)−P(1)	90.06(9)
O(2)−Ru(1)−P(1)	89.43(8)	P(1)−O(5)−C(43)	124.2(2)
Ru(1)−O(1)−C(21)	114.7(3)	Ru(1)−O(2)−C(22)	114.0(2)
O(1)−C(21)−C(22)	114.0(3)	O(2)−C(22)−C(21)	115.1(3)
O(1)−C(21)−O(3)	124.9(4)	O(2)−C(22)−O(4)	125.2(4)
O(3)−C(21)−C(22)	120.9(4)	O(4)−C(22)−C(21)	119.6(4)
C(44)−Si(1)−C(51)	110.68(17)	C(49)−Si(1)−C(50)	108.1(2)

Table 16S. Crystal data and collection details for **3·CH$_3$COCH$_3$**, **4**, **5** and **6·C$_6$H$_{14}$**.

	3·CH$_3$COCH$_3$	**4**	**5**	**6·C$_6$H$_{14}$**
Formula	$C_{33}H_{35}Cl_4O_3PRu$	$C_{28}H_{29}Cl_2OPRu$	$C_{34}H_{43}Cl_2OPRuSi$	$C_{42}H_{57}O_5PRuSi$
Fw	753.45	584.45	698.71	802.00
T, K	100(2)	100(2)	100(2)	100(2)
λ, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Triclinic
Space Group	*Pbca*	*Pbca*	$P2_1/c$	$P\bar{1}$
a, Å	18.174(3)	14.3504(8)	17.1191(8)	9.3525(8)
b, Å	13.861(2)	16.8861(9)	10.5238(5)	13.2672(12)
c, Å	25.670(4)	42.303(2)	18.4530(9)	16.7694(15)
α °	90	90	90	97.189(3)
β, °	90	90	100.9940(10)	93.247(3)
γ, °	90	90	90	101.528(3)
Cell Volume, Å^3	6466.7(18)	10250.9(10)	3263.4(3)	2015.6(3)
Z	8	16	4	2
D_c, g cm^{-3}	1.548	1.515	1.422	1.321
μ, mm^{-1}	0.898	0.902	0.756	0.500
F(000)	3072	4768	1448	844
Crystal size, mm	0.19×0.16×0.08	0.16×0.14×0.10	0.18×0.16×0.12	0.16×0.13×0.10
θ limits, °	1.587–25.099	1.715–25.049	2.238–25.999	1.228–25.048
Index ranges	$-21 \leq h \leq 21$ $-16 \leq k \leq 16$ $-30 \leq l \leq 30$	$-17 \leq h \leq 17$ $-20 \leq k \leq 20$ $-50 \leq l \leq 50$	$-21 \leq h \leq 21$ $-12 \leq k \leq 12$ $-22 \leq l \leq 22$	$-11 \leq h \leq 11$ $-15 \leq k \leq 15$ $-19 \leq l \leq 19$
Reflections collected	59384	119882	41769	23451
Independent reflections	5732 [R_{int} = 0.1620]	9074 [R_{int} = 0.2221]	6410 [R_{int} = 0.0612]	7122 [R_{int} = 0.0301]
Completeness to θ max	99.5%	100.0%	100.0%	99.8%
Data / restraints / parameters	5732 / 219 / 382	9074 / 168 / 601	6410 / 0 / 369	7122 / 44 / 429
Goodness on fit on F^2	1.223	1.172	1.114	1.052
R_1 ($I > 2\sigma(I)$)	0.1402	0.0956	0.0473	0.0527
wR_2 (all data)	0.2888	0.1788	0.0984	0.1345
Largest diff. peak and hole, e Å^{-3}	1.443 / –2.542	1.529 / –1.593	0.841 / –0.939	2.405 / –1.092